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British contributions to science, 1851–1951

PART TWO

The account given in our July issue of some British contributions to science during the century between the Great Exhibition of 1851 and the Festival of Britain in 1951 dealt mainly with astronomy, physics, and biology. The period includes also many notable achievements of British scientists in all departments of chemistry. It comprises, for example, the first recognition of valency—by Edward Frankland in 1852. During the earlier part of the period, this idea was for the most part applied in organic chemistry, but it served, too, as a unifying principle in the study of elements other than carbon. It gradually became clear, however, that the simpler views of valency which rendered such valuable service in organic chemistry were insufficient in the remaining field, and here the theory of co-ordination compounds, proposed by Alfred Werner of Zürich in 1893, acted as a guide. Significant contributions to the study of such compounds were made in the 1920's by Sir Gilbert Morgan, and an explanation of their structure in terms of the electronic theory was given by N. V. Sidgwick, who employed with much success the conception of a co-ordinate link as a special case of an ordinary valency bond. Cognate with theories of valency is the classification of the elements, and we may recall the tentative gropings towards the periodic system made by W. Odling and J. A. R. Newlands.

One of the most successful British workers in the realm of inorganic chemistry was Sir Henry Roscoe, whose researches on vanadium are models of chemical investigation. Sir William Crookes made an intensive study of the rare earths, and in 1861 discovered thallium. Later in the period came the romantic story of the discovery in the atmosphere of a whole family of new elements—the inert gases—as a result of the brilliant work of the third Lord Rayleigh, Sir William Ramsay, M. W. Travers, and others.

From the time of Davy and Faraday, physical chemistry has always had a strong attraction for British chemists. Chemical kinetics has been a favourite subject with them and is therefore selected for special mention here. In 1866, a year before the satisfactory enunciation of the law of mass action by the Norwegians C. M. Guldberg and P. Waage, the underlying idea had been used in a particularly noteworthy study by A. G. V. Harcourt and W. Esson at Oxford; their work may be said to have formed the basis, both in theory and in experiment, of the modern science of chemical kinetics. On the experimental side, useful contributions were made by J. H. Gladstone and the Irish scientist J. H. Jellett, while in the difficult region of gas reactions the work of H. B. Dixon, begun in 1884, was of fundamental importance. Incidentally, it may be remarked that Dixon's discovery of the curious influence of water on many chemical reactions, a discovery ably pursued by his pupil H. B. Baker, had considerable effect on theoretical views on catalysis. The study of gaseous explosions by Dixon was continued by W. A. Bone and R. V. Wheeler and is still engaging the attention of other British chemists. Our knowledge of chemical kinetics in general has in more recent years been advanced by such workers as Sir Cyril Hinshelwood and E. A. Moelwyn-Hughes, who have not only greatly added to the experimental data but have suggested theories commanding wide support.

Roscoe did not confine his interest to inorganic chemistry alone; he conducted much research on physico-chemical problems. His experiments on liquid solutions were of great accuracy, but it is perhaps his study of the action of light on chemical changes which is best known in this field. Early work on the action of light on the combination of hydrogen and chlorine was done by Dalton and by J. W. Draper (an Englishman who emigrated to America), but the work of R. W. Bunsen and Roscoe, begun in 1855, was in effect the foundation-stone of modern photochemistry. Photochemical work has been actively continued in Britain ever since.

The wide domain of colloid chemistry, opened by the pioneer researches of Thomas Graham, has been cultivated with conspicuous success by many later British chemists. Of outstanding workers on the subject, mention may be made of S. E. Linder and H. W. Picton, Sir William Hardy, and Sir Eric Rideal. Rideal, J. W. McBain, and N. K. Adam have also made notable contributions to the study of adsorption.

Limitations of space preclude a description of the part played by British workers in the development of other branches of physical chemistry, such as electrochemistry, thermochemistry and thermodynamics, and the phase rule, but it is not too much to say that it has won equal success.

A century ago, the development of organic chemistry had reached a particularly interesting stage. The fundamental problem of organic molecular constitution was approaching a solution. Liebig's earlier view of organic chemistry as the chemistry of compound radicals led up through many stages to the idea of mixed types, based by A. W. Williamson on work on ethers (1850–2). Frankland's theory of valency, already mentioned, was soon followed by A. Kekulé's recognition, in 1858, of the quadrivalency of carbon and the linking of carbon atoms. These ideas, and the related theory of organic molecular structure, were entertained simultaneously by the neglected Scottish chemist A. S. Couper. Both Kekulé and Couper put forward representations of organic molecules which bear a close resemblance to modern structural formulae. Crum Brown introduced graphic formulae in 1865, showing each individual valency bond. These structural representations of organic molecules, arising partly from the work and ideas of British chemists, have been mainly responsible for the amazing developments of pure and applied organic chemistry in the succeeding period.

In 1856, W. H. Perkin senior (later Sir William) obtained mauveine when trying to prepare quinine artificially. He later built the first dyestuffs factory, and the latent possibilities of coal tar as a source of unending synthetic dyes, perfumes, and fine chemicals of many kinds soon became apparent. The consequent flood of successful research was guided by the theory of organic molecular structure that had synchronized so closely with Perkin's original discovery.

In Britain, the development of organic chemistry owed much at this time to chemists who had been trained, between 1846 and 1864, at the Royal College of Chemistry, London, under the direction of A. W. Hofmann. Hofmann pictured England as becoming 'the greatest colour-producing country in the world,' but the temporary support of chemistry died down, and Hofmann left London for Berlin in 1864. Not until the war of 1914–18 came a public realization of the importance to Britain of a strong organic chemical industry, with a particular emphasis on the key industry of organic dyes.

In the half-century between Hofmann's departure and the first world war there was a remarkable expansion of academic organic chemistry, in which British chemists, although receiving little encouragement, played a worthy role. Among these investigators, most of whom occupied professorial chairs, such typical representatives come to mind as H. T. Brown in the chemistry of brewing, R. Meldola in the chemistry of dyes, W. H. Perkin junior in the terpene and alkaloid fields, F. S. Kipping in the organic chemistry of silicon, Sir Arthur Harden in bacterial chemistry, Sir William Pope in stereochemistry, and Sir James Irvine and Sir Norman Haworth in sugar chemistry.

In the subsequent period, astonishing progress has been made in these and other fields of organic chemistry. As illustrations of the outstanding achievements of British chemists it is sufficient to mention the contributions of contemporary workers, among whom Sir Robert Robinson is pre-eminent, in such diverse fields as the chemistry of alkaloids, anthocyanins, terpenes, steroids, sugars, complex carbohydrates, vitamins, natural pigments, synthetic dyes, phthalocyanines, high polymers, acetylenic compounds, stereochemistry, and the electronic interpretation of organic reactions.

Sir Frederick Gowland Hopkins' work on vitamins (1906–12) opened up a vast new field of primary importance, to which other British workers have made contributions of high value, including the first synthesis of a member of this class, vitamin C (1933). The discovery of adrenaline, the first hormone to be synthesized, may be traced back to the work of Sir Edward Schaefer and G. Oliver, in 1894, on the medulla of the adrenal gland. Sir William Bayliss and E. H. Starling's original recognition of a hormone (1902), the successful study by British investigators of the pituitary (1909) and thyroid (1914) hormones, and the isolation (1921) and manufacture of insulin, are landmarks in the development of this second field, in which the sex hormones and cortisone have provided new centres of interest. In a third field, original British work by Sir Alexander Fleming (1929) on the inhibiting effect of moulds on the growth of organisms, culminating in the British isolation and investigation of penicillin by Sir Howard Florey and E. Chain and the Anglo-American achievement of its commercial production during the second world war, has led to the study of streptomycin and other natural antibiotics of much significance in chemotherapy.

In the domain of synthetic drugs and chemotherapeutic agents, the earlier success of novocaine has been matched more recently by the elaboration in Britain of the sulphonamides, of Paludrine, and of an effective antidote to mustard gas. These achievements are to be welcomed as heralds of the approach of a rational system of therapeutics.

Carotenoids and vitamin A–the end of a chapter

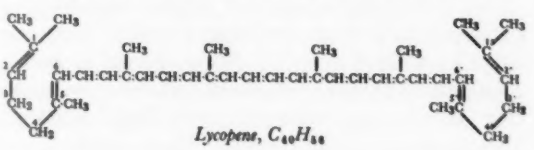
SIR IAN HEILBRON and A. H. COOK

The carotenoid pigments have excited attention from the very beginning of organic chemistry. The interest attached to many of them is heightened by their structural relationship to vitamin A and their probable role in living cells. A period of descriptive and analytical examination of the carotenoids has now reached a culminating point with the complete synthesis of vitamin A and of representative carotenoid pigments. The present article completes the story begun by Professor Paul Karrer in ENDEAVOUR, 7, 3, 1948.

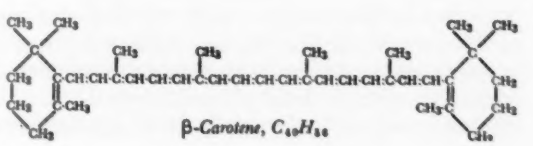
The carotenoids are, with few exceptions, highly unsaturated fat-soluble orange or yellow pigments. Representatives of them are widely distributed in nature. Typical substances of the class are the isomeric hydrocarbon pigments occurring in the carrot and elsewhere (carotenes), or in the tomato (lycopene), and pigments of different degrees of oxygenation such as cryptoxanthin, zeaxanthin, and lutein (xanthophyll), associated with the colours of the orange, maize, and egg-yolk respectively. Exceptional carotenoids include the water-soluble glycoside crocin, present in the yellow stamens of the crocus, and the blue protein-adduct ovoverdin, or astacene, occurring in lobster-shell.

As recently as two decades ago, the chemistry of this group was practically confined to knowledge of the molecular formulae of carotene, $C_{40}H_{56}$, which had been shown to consist of a mixture of isomerides, and of a few closely related representatives containing oxygen. That the ensuing years have revealed an exceptionally detailed picture of this field has been due to the development of microanalytical techniques, and the application of chromatographic adsorption. As a result, between eighty and one hundred structurally distinct natural carotenoids have so far been recognized; in addition many are known to be capable of assuming stereoisomeric forms, some of which, notably those of lycopene, are encountered in nature. The detailed chemistry of some of these pigments has previously been reviewed in this journal [1], so that only salient and novel features warrant attention in this account. Disregarding a few esters, such as the widely distributed heleniene, which is a dipalmitate of lutein, all the known carotenoids contain either 40 carbon atoms or a lesser number which can, in most if not all cases, be structurally related to the number in the more complex compounds. The constitutions of a few typical carotenoids are shown below; these illustrate the regular pattern of isoprene units and the polyene systems, mostly conjugated, which are characteristic features of the more complex carotenoids and which can be related to the structures of the simpler representatives. It will be seen that lycopene and β-carotene are isomeric, and that zeaxanthin and β-carotene have identical structures except for two hydroxyl groups characterizing the former. Such relations are common throughout the whole group of carotenoids. For example, α-carotene differs from β-carotene only in the transposition of one double bond from the 5:6 to the 4:5 position, putting it out of conjugation with the remainder of the polyene system; this feature is associated with the optical activity of the α-isomeride. Again, cryptoxanthin, $C_{40}H_{56}O$, contains only one of the two hydroxyls of zeaxanthin and is thus constitutionally intermediate between that compound and β-carotene; lycoxanthin, $C_{40}H_{56}O$, bears exactly the same relation to lycopene as cryptoxanthin does to β-carotene.

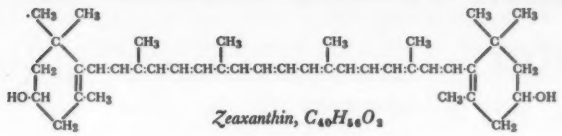
While it is unnecessary in the present article to attempt to detail the intricate work which led to the acceptance of these and many related structures, it is of more than passing interest to recall



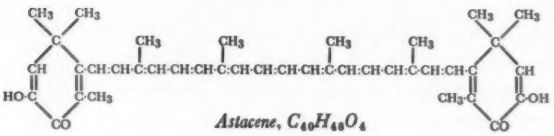
Lycopene, $C_{40}H_{56}$



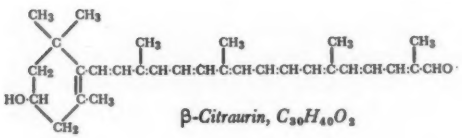
β-*Carotene*, $C_{40}H_{56}$



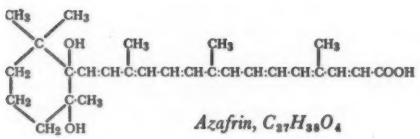
Zeaxanthin, $C_{40}H_{56}O_2$



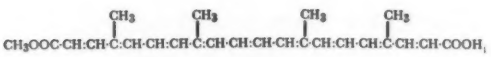
Astacene, $C_{40}H_{48}O_4$



β-*Citraurin*, $C_{30}H_{40}O_2$



Azafrin, $C_{27}H_{38}O_4$

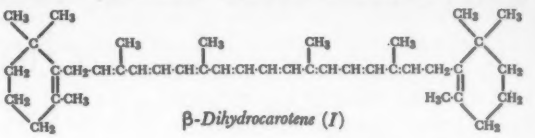


Bixin, $C_{25}H_{30}O_4$

Crocetin, $C_{20}H_{24}O_4$

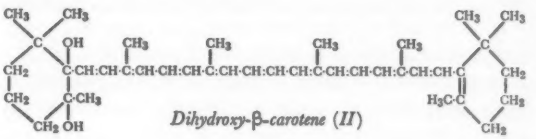
that the polyene system as it occurs in the carotenoids remains one of largely unknown potentialities. A glimpse of the chemical reactivity of this grouping is, however, afforded by several reactions which have come to light incidentally.

For example, while the highly unsaturated, conjugated chain is—not unexpectedly—very sensitive to air and other oxidizing agents, as well as to reducing agents, restrained reductive or oxidative attack may lead to controlled structural alteration at specific points. Thus, reduction of β-carotene in ethereal solution by means of aluminium amalgam leaves the terminal di-tertiary double bonds unaffected, but adds a hydrogen atom to each end of the residual conjugated system to give a β-dihydrocarotene (I) [2], a substance which has recently been synthesized:

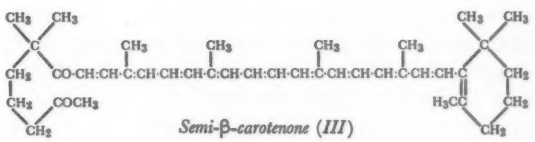


β-*Dihydrocarotene* (*I*)

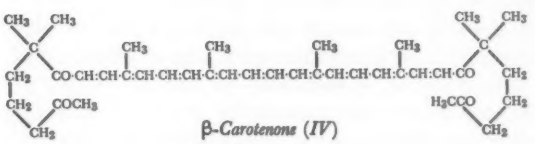
On the other hand, controlled oxidation by means of chromic acid leads first to attack at one of the double bonds in the ring, with the formation of dihydroxy-β-carotene (II), and then to attack at the other terminal double bonds, ultimately giving β-carotenone (IV), semi-β-carotenone (III) being formed as an intermediate.



Dihydroxy-β-carotene (*II*)

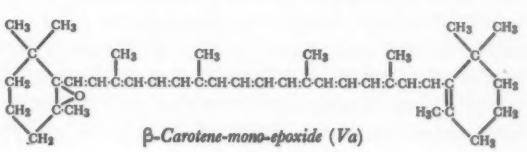


Semi-β-carotenone (*III*)

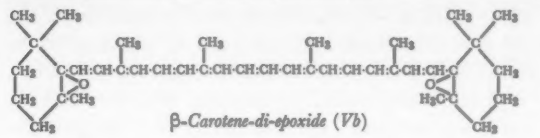


β-*Carotenone* (*IV*)

It is worth recalling that it was an extension of such reactions which led to the recognition of the structural relationship between β-carotene on the one hand, and azafrin, as well as bixin and certain other carotenoids, on the other. Still more significant, perhaps, was the discovery that oxidation of carotenoids by per-acids results in many instances in the addition of oxygen to the double bonds of the ionone rings. So far, only β-ionone rings have been observed to be attacked in this manner, one or two oxygen atoms being taken up according to the nature of the terminal groups present. The products, where perbenzoic or perphthalic acid is used, usually have the properties of 1:2-epoxides [3]; for example, β-carotene yields both a mono- (Va) and a di-epoxide (Vb):



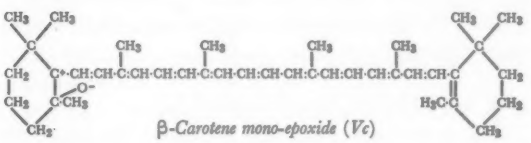
β-*Carotene-mono-epoxide* (*Va*)



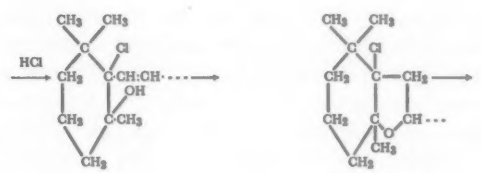
β-*Carotene-di-epoxide* (*Vb*)

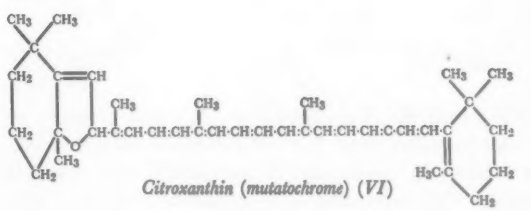
It is probably significant for the understanding of the biological role of the carotenoids that several naturally occurring pigments, such as trollixanthin [4], have been shown to be epoxides. Again, antheraxanthin, one of the characteristic pigments of the anthers of *Lilium tigrinum*, is indistinguishable from zeaxanthin mono-epoxide; violaxanthin from the yellow pansy is identical with zeaxanthin di-epoxide.

The carotenoid epoxides are very sensitive to mineral acids, a fact which has suggested that the normal epoxide formulation may advantageously be replaced by a polar representation, as in Vc. When carotene mono-epoxide is treated with hydrogen chloride it is converted partly into β-carotene, but to a major extent into another pigment called mutatochrome; this is a substance identical with the citroxanthin (VI) which occurs in orange-peel [5]. Mutatochrome contains a fused furanoid structure, and the origin of the latter is most easily understandable on the basis of the modified epoxide formulation indicated below:



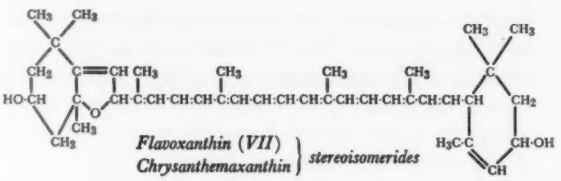
β-*Carotene mono-epoxide* (*Vc*)





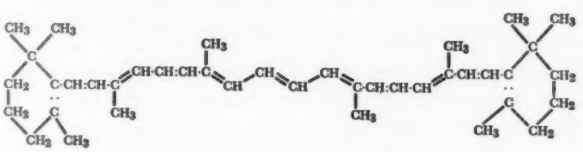
Citroxanthin (*mutatochrome*) (*VI*)

Presumably the furanoid carotenoids, like the epoxides, are also widely distributed in nature. Auroxanthin, a pigment of the yellow pansy, is the difuranoid compound structurally derived from zeaxanthin di-epoxide, while flavoxanthin (VII), the pigment of the flowers of the dandelion, is similarly related to the mono-epoxide of lutein, as also is chrysanthemaxanthin, present in gorse flowers; the latter pigment therefore appears to be stereoisomeric with flavoxanthin.



Flavoxanthin (*VII*)
Chrysanthemaxanthin } *stereoisomerides*

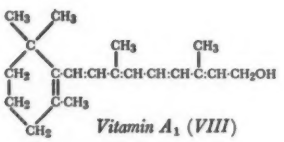
The symmetrical formula of β-carotene contains eleven double bonds, of which it is concluded, on theoretical grounds, that only five, as indicated by full lines in the formula below, are capable of adopting more than one configuration [6]. These are depicted in the formula as having a uniformly *trans*-configuration, but a considerable number of *cis*-configurations may be foreseen. In fact, β-carotene and many other carotenoids have been artificially obtained in several of the possible forms, and several *cis*-carotenoids are known to occur naturally.



The carotenoids are primarily plant pigments; as far as is yet known the animal organism is unable to synthesize materials of this class, or to do more than effect limited modifications in the structures of those members of it which are ingested. Despite this fact, more is known of the significance of certain carotenoids in the animal kingdom than of their importance to plant life. The universal occurrence of the carotenes and other carotenoids—singly or as mixtures—in green leaves has led to suggestions that these pigments play some essential part in photosynthesis. Again, the appearance of unusual carotenoids in individual organs, such as that of α-carotene in the spermatozoids of *Fucus* species, has prompted the

suggestion that the pigmentation is associated with the motility or the chemotactic sensitivity of the gametes [7]. In the latter connection, the ready formation of epoxides by many carotenoids, and the ease with which the epoxide oxygen atom is lost, inevitably stimulate speculation on a possible mechanism of oxygen transport. In a fascinating series of experiments, Kuhn and Moewus have drawn attention to the part which appears to be played by crocin, *cis*- and *trans*-crocetin, and several related substances, in conditioning the fertility and in bringing about the fertilization of the gametes of selected *Chlamydomonas* species [8]. Many of the above suggestions, however, are either without adequate experimental foundation or pose more queries than they seem to answer.

In the animal kingdom a close connection between carotene and a growth factor was suspected more than thirty years ago, and as the chemistry of the fat-soluble vitamins evolved it became apparent that a relationship existed between carotene and vitamin A [9]. Later, it was shown that pure β-carotene could act as a substitute for vitamin A_1, and it is now recognized that, in fact, β-carotene supplies a major part of the vitamin A requirements in human diet. Other carotenoids may be less efficient substitutes; for example, α- and γ-carotenes have only half the effectiveness of the β-isomer, a relation upon which recent work has thrown light [10]. Vitamin A_1 has been shown to have structure (VIII), and a relationship between this structure and those of the known carotenoid provitamins may be clearly discerned.



Vitamin A_1 (VIII)

Thus, formally, two molecules of vitamin A_1 may be considered as arising from the hydrolytic fission of β-carotene:

$$C_{40}H_{56} + 2H_2O \rightarrow 2C_{20}H_{29}OH.$$

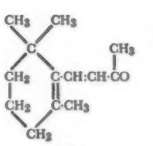
A similar fission of α- or γ-carotene, or indeed of any carotenoid containing an unsubstituted β-ionone ring, could, formally, lead to the formation of only one molecule of vitamin; the latter requirement is encountered, for example, in cryptoxanthin, which actually has only half the effectiveness of β-carotene as a provitamin A_1. These comparatively simple relationships are, incidentally, affected by the steric configurations of the carotenoids concerned, *cis*-isomers proving to be less effective than parent compounds entirely *trans*.

The conversion of β-carotene into vitamin A_1 has been realized experimentally, but despite the apparent simplicity of the change concerned, no results capable of being utilized on a large scale have so far emerged [10]. The desirability of directly synthesizing vitamin A_1 industrially, to supplement that available from fish-liver oils, is therefore a very important problem. During very recent years, this synthesis has been achieved by the ingenuity of the organic chemist, notably by methods involving the use of acetylenic intermediates. It is not surprising that suitable extension of the same methods has led also to the synthesis of a variety of carotenoids; some impression, necessarily brief, of these developments is given in the latter part of this article.

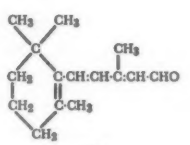
Before finally leaving the question of the physiological significance of the carotenoids, mention must be made of their part in the process of vision. Though their detailed role is still unelucidated, it has been found that visual purple (rhodopsin) is a protein-retinene complex from which, on exposure to light, the retinene component is liberated. Constitutionally, this component is the aldehyde corresponding to vitamin A_1, into which it is converted [11] in the visual process. Conversely, vitamin A_1 becomes transformed in the dark into retinene and thence into visual purple.

THE SYNTHESIS OF VITAMIN A_1

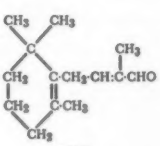
The two obvious starting materials for any synthesis of the vitamin are β-cyclocitral and β-ionone (IX); only the latter has proved sufficiently reactive to be useful. The first synthesis of impure vitamin A_1 was achieved in 1937 by converting



(IX)



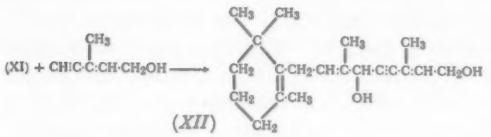
(X)



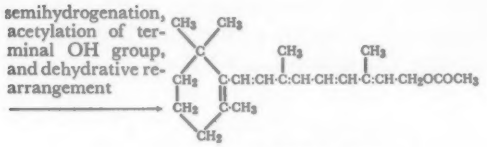
(XI)

(IX) into the C_{15} aldehyde (X) and thence, by condensation with β-methylcrotonaldehyde, into vitamin A_1 aldehyde, from which the vitamin itself was obtained on reduction [12]. This method leaves much to be desired, and far more fruitful has been the exploitation of the related C_{14} aldehyde (XI) obtained as the ultimate result

of condensing β-ionone with ethyl chloracetate. It was thought [13] that condensation of this aldehyde with 3-methylpent-2-en-4-yn-1-ol (XII) perhaps offered a route to the vitamin by steps such as the following:



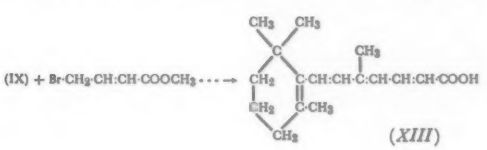
(*XII*)



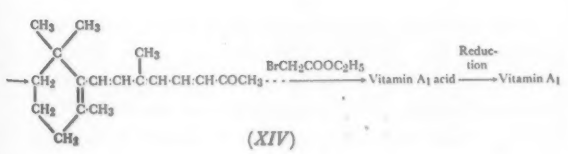
Vitamin A acetate

At the time of these suggestions (1942) the feasibility of the projected reactions had been foreshadowed, but a considerable volume of exploratory work on the preparation and reactions of acetylenic intermediates had still to be carried out. Ultimately, in 1946, the synthesis was realized, thanks in great measure to an intensive study of the reactions leading to the key intermediate (XI). A crystalline alcohol identical in all respects with the natural vitamin was eventually obtained [14]. It may be pointed out that this type of synthesis is applicable to a variety of isomerides, analogues, and derivatives of the vitamin, and that several of these have in fact been prepared.

Another series of reactions, using β-ionone as the starting material, includes its condensation with methyl γ-bromocrotonate to give ultimately the C_{17} acid (XIII) and thence, by means of dimethyl-cadmium or methyl-lithium, the C_{18} ketone (XIV). A second Reformatsky reaction, using ethyl bromacetate, then yields vitamin A_1 acid [15]; thence the vitamin itself is obtained by reduction with lithium aluminium hydride.



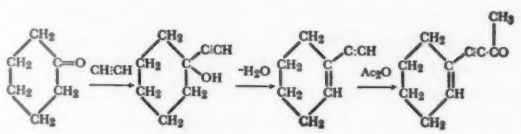
(*XIII*)

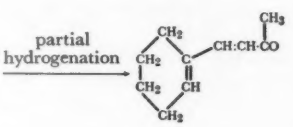


(*XIV*)

Vitamin A_1 acid is of particular interest because, although its biological activity is comparable with that of the vitamin itself [16], it does not appear to be stored in the liver.

The preceding syntheses, flexible though they are, obviously do not permit of varying the structure in the β-ionone part of the molecule. This can be accomplished only by starting with synthetic analogues of β-ionone. Perhaps the most useful of such approaches so far devised consists in the dehydration under selected conditions of ethynylcyclohexanol or its substituted derivatives, followed by Grignard condensation of the product with acetic anhydride:



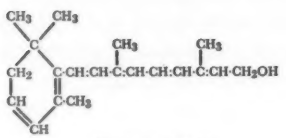


Application of the methods outlined earlier, or of extensions of them, has provided a variety of vitamin A_1 analogues, though the biological activity of the products was exceedingly small [16].

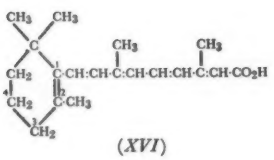
VITAMIN A_2

It has been recognized for some years that the liver oils of fresh-water fish contain, in addition to vitamin A_1, a second vitamin of similar structure, now known as vitamin A_2. Several conjectures were made as to the structure of the latter vitamin, though precise work was difficult or impossible in the absence of pure material; even in very recent years there has been no agreement on the empirical formula of the compound. An early suggestion that it may be represented as a 3-dehydrovitamin A_1 (XV) has now received unexpectedly ready confirmation [17]. Vitamin A_1 acid (XVI), in the form of its methyl ester, gave a 3-bromo-derivative on treatment with N-bromosuccinimide. This product readily suffered dehydrobromination, and on reducing the free acid (XVII) with lithium aluminium hydride an oil was obtained which, in physical and general chemical properties, was virtually indistinguishable from vitamin A_2. For example, on oxidation it was converted into a retinene$_2$ which showed

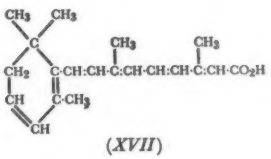
light absorption similar to that of a retinene$_2$ prepared from natural vitamin A_2; it seems, however, that the incidence of *cis-trans* isomers hinders any simple identification of the aldehydes, or indeed of the parent alcohols. It is interesting to recall that in the case of vertebrates utilizing vitamin A_2 the part of retinene$_1$ is played by retinene$_2$ or vitamin A_2 aldehyde; in these instances also the visual purple consists of a protein complex, porphyropsin, of vitamin A_2 aldehyde [18].



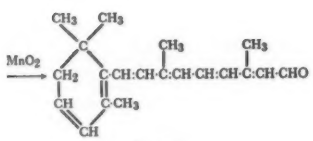
Vitamin A_3 (XV)



(XVI)



(XVII)



Retinene$_3$

THE SYNTHESIS OF CAROTENOIDS

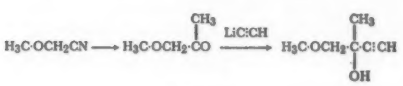
The synthesis of structures of the complexity and sensitivity of the carotenoids offers an immediate challenge to the ingenuity of the chemist. It is clear, especially when the symmetrical structures of β-carotene and certain other carotenoids are considered, that many of the approaches to vitamin A already outlined offer possible synthetic routes to the pigments themselves, and it has been pointed out [19] that a number of possibilities present themselves for the elaboration of the C_{40} skeleton. For example, limiting attention to intermediates whose preparation has already been effected, or for which preparations might be devised without great difficulty, the elaboration of β-carotene may be envisaged as proceeding in the following steps:

$$C_{14} + C_5 \rightarrow C_{19}; \qquad 2C_{19} + C_2 \rightarrow C_{40}.$$

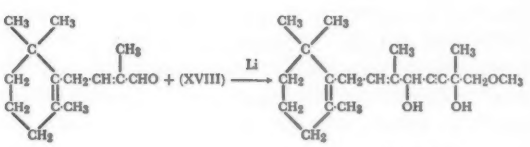
A second approach is represented by:

$$C_{13} + C_3 \rightarrow C_{16}; \qquad 2C_{16} + C_8 \rightarrow C_{40}.$$

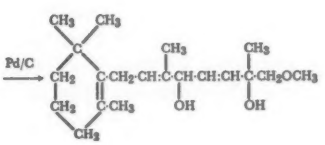
In the first of these possibilities the C_{14}-aldehyde which had already figured prominently in the synthesis of vitamin A_1 promised to be the most satisfactory starting material. We need not detail the arguments leading to the selection of the C_5 component, but the aldehyde, on condensation with the carbinol (XVIII), did in fact afford the diol (XIX), which was semi-hydrogenated and the product smoothly dehydrated. From the resulting mixture there was isolated a vinyl ether (XX), treatment of which with dilute acid afforded the desired C_{19} aldehyde (XXI):

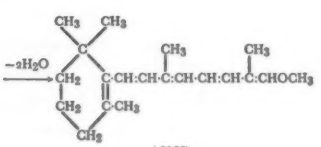


(XVIII)

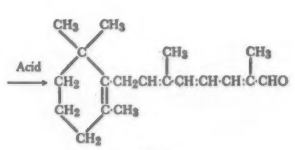


(XIX)





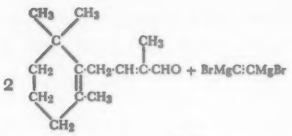
(XX)



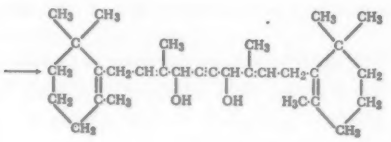
(XXI)

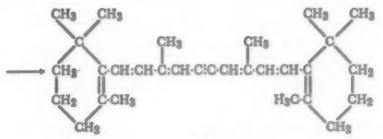
Unsaturated aldehydes, simpler than, but comparable with, (XXI), had already been doubly condensed with the *bis*-Grignard reagent derived from acetylene. For example, two molecules of the C_{14} aldehyde (XI) and one of acetylene had

afforded the C_{30} hydrocarbon (XXII), while the C_{18} aldehyde (XXIII) similarly yielded a C_{38} hydrocarbon. Direct or indirect hydrogenation of these acetylenic compounds converted them into the completely conjugated ethylenic hydrocarbons of carotenoid character [20] such as (XXIV).

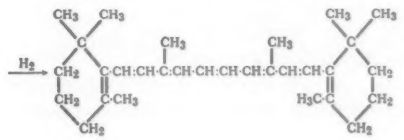


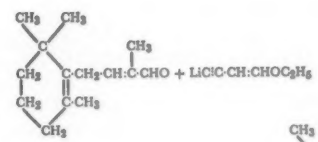
(*XI*)

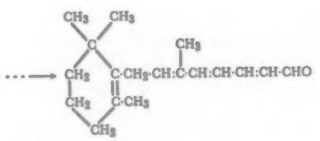




(*XXII*)





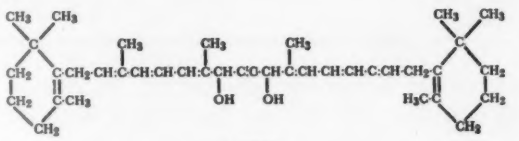


(*XXIII*)

(*XXIV*)

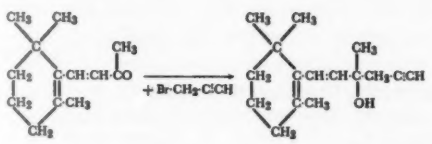
(7:7)-*Bis-desmethyl-β-carotene*) [21]

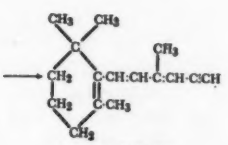
The way was now clear for the new C_{19} aldehyde (XXI) to be condensed with acetylene dimagnesium bromide to give primarily the C_{40} diol (XXV); ultimately β-carotene, identical in all respects with the natural pigment, was obtained [22]:



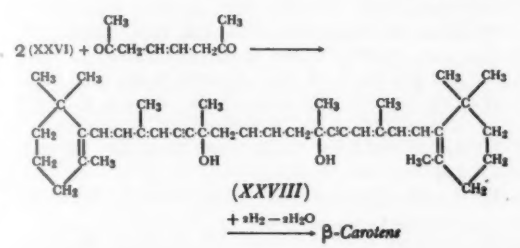
(*XXV*)

The alternative approach to the carotene structure, mentioned above, has also been realized in the following manner. The C_{16} component was the acetylenic hydrocarbon (XXVI) derived from β-ionone, two molecules of which were condensed with 4-octene-2:7-dione (XXVII) [23] to give the C_{40} di-ine diol (XXVIII). In the now familiar way, addition of hydrogen to the two acetylenic groups, followed by dehydration, again afforded β-carotene:





(*XXVI*)

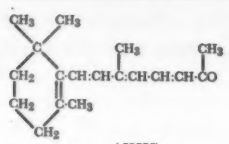


(*XXVIII*)

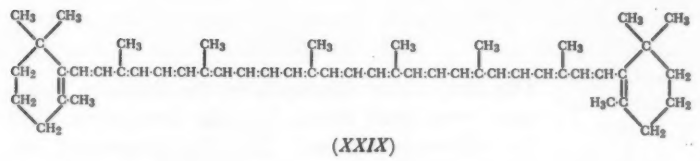
β-*Carotene*

A similar series of reactions, beginning with the open-chain γ-ionone, has provided a complete synthesis of lycopene [24], while γ-carotene and α-carotene have likewise been obtained from appropriate starting ketones.

The flexibility of these syntheses has paved the way to a variety of artificial carotenoid pigments. For example, by beginning not with α- or β-ionone but with the analogous C_{18} ketone (XIV), hydrocarbons with 15 conjugated double bonds have been prepared, as in 'decapreno-β-carotene' (XXIX) [25]:



(*XIV*)



(*XXIX*)

from the time of Berzelius. Recently, however, the chemistry of natural polyene compounds has assumed a new appearance. The picture, from the chemical, and particularly from the synthetic, standpoint, was formerly one of increasing complexity; now, largely as a result of intensive study of the potentialities of acetylenic chemistry, the major synthetic problems have been overcome, and, with the conclusion of this phase, attention will undoubtedly be increasingly directed to the role of these substances in the living cell. The organic chemist has had success; now perhaps it will be the turn of the biochemist to uncover a further section of the picture. It may be that a glimpse of this new chapter is already afforded by recent work on the isolation of 5-ketotetrahydroionone and related compounds from urine [26] since it seems that they are transformation products of carotenoid precursors.

CONCLUSION

The striking results here briefly described bring to a close one of the most fascinating stories in the chemistry of natural substances. The opening phases take us back more than a century, for various aspects of the study of carotenoids have claimed the attention of outstanding scientists

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Sexual dimorphic colour characters in animals

H. G. VEVERS

The morphogenetic processes underlying the secondary sexual differences of colour in animals, which have long been recognized as playing an important part in the evolution of species, have received much attention in recent years. Two distant types of coloration have been shown to be involved, one due solely to pigment and the other to refractive effects. Coloration may, in some cases, be under direct genetic control; in others, hormones play a decisive part, so that often male coloration can be induced in females, and *vice versa*.

The selective value of sexual dimorphic characters has been the subject of much discussion since the postulation by Darwin [4] of a theory of sexual selection, and the subject was considerably clarified by the valuable analysis of J. S. Huxley [6]. The discussion is concerned primarily with the means by which sexual dimorphic characters have developed during the evolution of a species. In recent years, however, there has been much work on the elucidation of morphogenetic processes responsible for the development of such characters during the life of an individual. These processes are necessarily closely linked with those involved in the general field of sex determination and sex differentiation.

Sexual dimorphism in animals is usually expressed in differences between the sexes in the colour, shape, or size of various external organs. It is difficult to draw a satisfactory distinction between this type of sexual dimorphic character and those, such as claspers and various types of copulatory organs, which are directly concerned with mating and gamete conjugation; these two groups are often conveniently termed secondary sexual and accessory sexual characters respectively. The present discussion is restricted to the phenomenon of secondary sexual differences in colour.

Colour in animals is most commonly caused by the reflection of incident light of certain wavelengths from a layer of pigment deposited in the surface tissues; this type of reflection gives normal pigmentary colours. There are, however, many animals in which the colour reflected by the pigment is markedly modified by an overlying layer of complex structure, giving the structural colours such as occur in some blue butterflies and in different iridescent colours. The pigments occurring in animals may belong to one of a number of chemical groups, but those responsible for sexual dimorphic colour characters are usually either melanins or carotenoids, which occur in most animal phyla, or pterins, which supply the wing pigments of many insects. In addition, many sexual colour characters involve the presence of structural colours, one sex being coloured by pigments only and the other by pigments with an overlay of 'structure.' Such structural layers may consist of a medium made turbid by ultramicroscopic spaces giving Tyndall blues, or of a surface-film structure giving iridescent colours of the type seen in a drop of oil spread out on water.

Sexual dimorphism in colour is almost unknown among the less specialized invertebrates, but occurs commonly in the insects. In some of the British blue butterflies ('*Polyommatini*') the difference in colour between the sexes is caused by the presence of structural layers in the wing scales. In the silver-studded blue (*Plebejus argus*) the female is drab brown in colour, being pigmented with melanin, whereas in the bright blue of the male's wings melanin pigmentation is overlaid by structural modifications in the scale surfaces. In transmitted light the wing appears dark brown.

The control of these sex characters in insects is genetic, and there is no evidence that hormonal factors play any part.

In fishes, sexual dimorphism in colour occurs most frequently among some of the tropical species, many of which are successfully kept and bred by aquarists in Britain. However, some species which are commonly caught along the British coasts show the phenomenon just as well as those from warmer waters. In the cuckoo-wrasse (*Labrus mixtus*), the male is yellow or orange with five or six bands of bright blue stretching backwards from the eye. The fins are yellow with a large blue spot on the dorsal fin. The female is

soft red-brown on the back, but lacks the blue bands entirely. It has, however, two black spots on the back near the dorsal fin, and a third similar spot near the tail. The yellow of the male and the red-brown of the female are both carotenoid colours, but no work has been done to show whether they are chemically identical. It is, in fact, possible for two different colours to be produced by the same carotenoid; in such a case it is usual for a red or yellowish colour to be produced by the free carotenoid, and for the other colour, which may be blue or green, to be produced by the same carotenoid linked with a protein radical. The blue of the male cuckoo-wrasse is produced by melanin with an overlay of structure, and the black spots of the female by melanin alone. This fish occurs in many coastal areas of Britain, more particularly in rocky areas. Further out, in the trawling grounds of the English Channel, large numbers of the dragonet (*Callionymus lyra*) are caught. This species shows very striking sexual dimorphism. The painting (plate 2) of the related *Callionymus reticulatus*, a species which has recently been rediscovered in trawl catches off Plymouth, shows the extent of the sexual colour and pattern differences. In the dragonets, the bright coloration of the male becomes fully developed only at the onset of the breeding season, but mature males can always be distinguished from females by some colour differences, as well as by the greater development of the snout and dorsal fin rays.

In birds, sexual differences in colour and other characters are widespread, and many examples can be found among wild and domestic species in Britain. In the common fowl, sexual dimorphism in colour occurs in the comb and wattles as well as in the plumage. The enlarged comb and wattles of a domestic cock are conditioned by the testis secretions, for the small, poorly developed comb of a young male will enlarge if the bird is given injections of a male hormone such as testosterone. On the other hand, the plumage of domestic fowls is modified by the action of ovarian hormones, for it can be shown that the dull plumage of the brown Leghorn hen appears only in the presence of ovarian secretions, and that the plumage of an ovariotomized female (or poulard) is similar to the bright plumage of a normal male, or of a capon. Furthermore, a capon injected with an ovarian hormone throughout a feather-growth period develops a female type of plumage more or less indistinguishable from that of the normal hen.

In the domestic fowl, therefore, sexual dimorphism in the colour and pattern of the feathers is maintained by the action of oestrogens on the developing feather germs. It is, however, not possible to generalize on sexual dimorphic plumage from this one example, because even the members of a related group, namely pheasants, do not behave in exactly the same way. It has been found that, as in the case of the domestic fowls, the dull coloration of the hen pheasant appears only in the presence of ovarian hormones, and, further, that hen pheasants with ovarian deficiencies tend to assume a male type of coloration. Similarly, in a cock or a caponized pheasant injected with an oestrogenic hormone, the feathers growing during the period of the treatment will be female in colour, but they do not assume all the pattern-details of a normal female feather. In particular, there is a difference in the angle which the colour bars make with the shaft. This can be seen in plate 1, in which (m) shows the normal female back feather of an Amherst pheasant, while (k) shows a back feather grown on a male Amherst pheasant receiving daily doses of oestrone. Similar feathers grown in two other feather tracts are also shown in plate 1.

The colours shown by the two barred feathers (plate 1, k and m) are dark brown and light brown, and are produced by different stages of oxidation of melanin. These colours are purely pigmentary, and the reflection from the surface is dull. On the other hand, in the normal male back feather (plate 1, g) and in the dark bars of the male pendent feather (a), the reflection is iridescent, and the main colour is a dark green. Here the pigmentary colour, a melanin deposited in the barbules, is overlaid by a thin film structure. In these iridescent male feathers the barbules are twisted on their own axis and present their broad flat sides to the observer, whereas in the matt female feathers there is no torsion of the barbules, which present their narrow upper edges. This is in itself an interesting sexual dimorphic character, and like the colouring of the back feathers it is controlled by ovarian hormones. As the dose of oestrone increases, the back feathers of a male Amherst pheasant show less and less torsion of the barbules, until with the larger doses (k) the barbule structure is indistinguishable from that of the homologous barbules in a normal female back feather.

In pheasants, therefore, some sexual dimorphic characters, such as barbule torsion, feather colour, and to a certain extent feather size, appear to be controlled by hormonal factors, but other

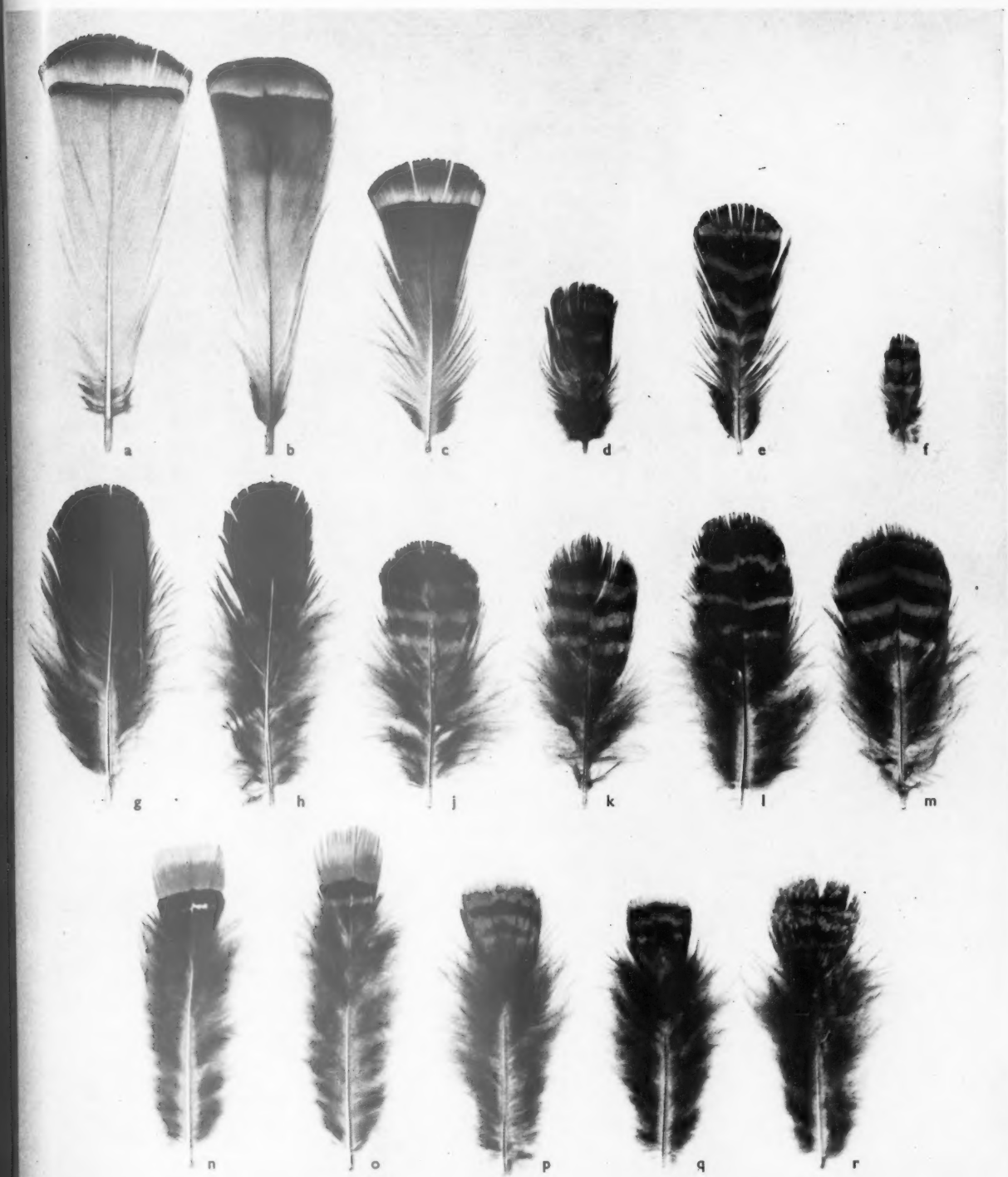

PLATE I – *The effect of varying doses of oestrone on the colour and pattern of feathers from three tracts of the male Amherst Pheasant. Top row, pendent tract; middle row, back tract; bottom row, saddle tract.* (a), (g), *and* (n) *Normal male feathers;* (b), (h), *and* (o) *feathers grown on male receiving* 2·5 γ *oestrone per day;* (c), (j), *and* (p) *feathers grown on male receiving* 10 γ *oestrone per day;* (d) *and* (k) *feathers grown on male receiving* 50 γ *oestrone per day;* (e), (l), *and* (q) *feathers grown on male receiving* 100 γ *oestrone per day;* (f), (m), *and* (r) *normal female feathers.*

PLATE 2 – Callionymus reticulatus C. & V. *Figures* 1 *and* 1a *show in lateral and dorsal view a male,* 108 *mm in length, which was caught off Plymouth on* 11*th May,* 1950. *Figures* 2 *and* 2a *show a female. (From an original coloured drawing by A. Fraser Brunner.)*

dimorphic characters, in particular the details of the barring patterns, are independent of the hormones and are probably under genic control. This method of sex differentiation has been referred to by some writers as the pheasant type to distinguish it from the hen type, where sexual dimorphic characters appear to be entirely controlled by hormonal factors. There is, however, among birds yet a third method of sex differentiation, which is usually termed the sparrow type. In many passerine birds it has been found that the sex hormones have no effect on the differentiation of sexual dimorphic plumage types. Thus Crew and Munro [2] have shown that control of the plumage is entirely genetic in the Gouldian finch (*Gouldaeornis gouldiae*), a coloured Australian species with pronounced sexual dimorphism.

The sparrow or insect type of control allows the appearance of clear-cut gynandromorphic animals, in which one side of the body shows male, and the other female, characters. In passerine birds and in insects an abnormal lateral sex-chromosome distribution early in development may lead to one side of the adult being genetically male while the other side is genetically female. This happened in the two Gouldian finch gynandromorphs described by Crew and Munro [2], where there is a clear line of demarcation in the plumage between a male and a female side. Similarly, it is not uncommon to find gynandromorphic insects. Ford [5] has published figures of gynandromorphic butterflies, including one of a particularly striking case in the common blue (*Polyommatus icarus*), in which the left side is female in coloration and the right side male.

Among domestic fowls, birds have been described in which the two sides of the body differ in size, and this lateral asymmetry has been attributed by Crew and Munro [2] to abnormal autosome distributions. These birds, however, are not necessarily sexually abnormal, and it is difficult to see how a true gynandromorph could appear in the fowl. Any bilaterality of sex-chromosomes in the cells of the skin would be masked by hormonal factors, and the whole plumage would be female in the presence of a functioning ovary, and male in its absence. There are, of course, cases where old hens with atrophied ovaries show patches of cock-type feathers. This is because the feather tracts have different thresholds of response to the oestrogenic hormones.

In the intermediate pheasant type of sex differentiation it is conceivable that a bird might appear with some degree of bilateral asymmetry of plumage. If it had an ovary, one side would have normal female feathers and the other would have intersexual feathers—female in colour but not in pattern. If, on the other hand, the bird had no functioning ovary, one side (with female sex-chromosome distribution in the skin cells) would have intersexual feathers—male in colour but not in pattern—and the other (genetically male) side would have normal male feathers. These four types of feathering have been produced experimentally in the common pheasant (Danforth [3]) and in the Amherst pheasant (unpublished data), but the nearest approach to a natural gynandromorph is the common pheasant first described by Bond [1] and re-examined by Huxley and Bond [7].

The development of sexual colour characters is, in fact, but one of the processes involved in sex differentiation. The determination of the primary sex is controlled by the genetic constitution of the individual, that is, by the quantitative supply of sex-chromosomes. If the embryo has only one X chromosome, it will develop in mammals into a male, and in birds and butterflies into a female, while the presence of two X chromosomes will determine the opposite sex. In some animals, such as insects and passerine birds, the sex-chromosomes continue to exert an effect throughout life by controlling the differentiation of sexual dimorphic characters, whether in colour or other attributes. In other groups of animals the sex-chromosomes determine the primary sex of the genital glands, and the secretions of these glands then control the course of future sex-character differentiation. The existence of an intermediate type of sex-character control in the pheasants does, however, suggest that there may be other animals with a similar type of control.

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Chemical identification by a physical method

MARY W. PORTER

For more than a century it has been recognized that the constancy of the interfacial angles of crystals provides a means of identifying them. By 1912, an index of some ten thousand different crystals had been prepared by Fedorov, but his system proved too complex for general use. The development of a simpler system was begun in Britain by T. V. Barker, and since his death in 1931 has been continued at Oxford. The first volume of data for use with this system has just been completed; it is an outstanding event in the history of chemical analysis.

It is well known that many crystals are bounded by plane faces, often with highly reflecting surfaces. The angles between these faces are characteristic of the chemical substance, and as early as 1669 Nicolaus Steno proved 'the constancy of angles' in measuring the angles of cross-sections of quartz. The first measurements of crystal angles were, of course, made by rather crude methods, but early in the last century goniometers were devised expressly for measuring the angles between crystal faces. The first two-circle goniometer was devised by W. H. Miller in 1874. Modern goniometers can measure angles with an accuracy of a few seconds of arc.

Since the angles of many thousands of substances have been accurately measured and recorded in the scientific literature, it would seem that in these measurements the chemist has a means of identifying a large number of substances. Why is it that he has hitherto been unable to make practical use of this apparently simple method of identification? The difficulty lies in the fact that many crystals are rich in faces and therefore have many interfacial angles. For purposes of identification it is obviously essential that, with a given substance, the same angle (or angles) shall always be taken as the classification angle(s). How is it to be decided which shall be chosen? The symmetry of the crystal does not necessarily settle the choice.

A somewhat crude illustration of the difficulty may be seen in figures 4–6. These figures represent the same crystal, acecaffin, drawn in different positions. Three crystallographers in different laboratories may each select a different north-pole position from which to measure and describe this crystal, and a different set of angles will be obtained in each case. If, by chance, all three select the same position, a second difficulty may still remain. The crystal may be rich in faces. Which of these faces shall be treated as the unit face to which the positions of the remaining faces may be referred? Figure 7 shows the terminating faces of a natural topaz crystal; figure 8, in which it is easier to see the problem, shows the same crystal ideally developed. It is necessary to decide which of the faces 7, 8, or 9 shall be accepted as the unit face.

A number of crystallographers have studied the problem of how the unclassifiable crystal measurements existing in the literature could be converted into an index of angles unambiguously applicable to the identification of chemical substances. In 1842 Frankenheim [3] classified 700 substances according to an archaic form of axial ratios; this work remained unnoticed except by T. V. Barker [4]. Later, a remarkable and extensive attack upon this problem was made by E. S. von Fedorov, professor in the School of Mines at St Petersburg (Leningrad). His method, which was based on theories of crystal structure, proved successful. In 1902, crystals of 50 substances, varying in their degree of chemical complexity, were sent to Fedorov from England for identification. Each was in a separate tube, numbered but unnamed. Fedorov measured the crystals and sent back 48 correct identifications. Crystals in the 49th tube were too ill-formed for measurement, and the 50th tube contained a substance which was not in his index, and which had, indeed, never previously been examined crystallographically [5]. The two substances shown in figures 1 and 2 were identified by the Fedorov method.

Barker achieved a notable success with Fedorov's method when he was sent by Dr Govaerts a crystal of unknown composition which had been removed from the intestines of a soldier. This crystal is shown in figure 1; its actual

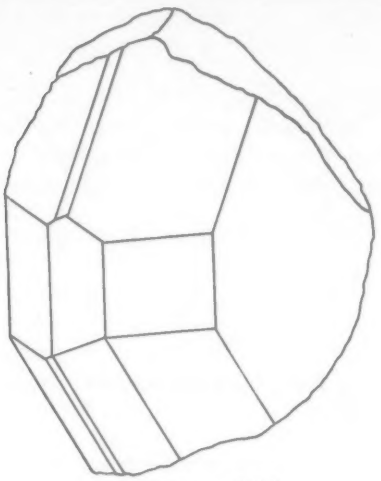

FIGURE 1 – *Salol.*

dimensions are 9 × 7½ × 4·5 mm and its weight 0·229 g. The front of the crystal is well developed, with clearly defined crystal faces; the back is rounded. After an investigation lasting 65 minutes, and without recourse to chemical analysis, Barker identified the substance as the drug salol (phenyl salicylate). A simple confirmation of this diagnosis was made by a melting point determination with a splinter of the crystal weighing less than 100 μg; the optical properties of the resolidified material were examined under the microscope [1].

Figures 2 and 3 show crystals of struvite ($NH_4MgPO_4.6H_2O$), found in the lungs of a dissected subject. These crystals were identified

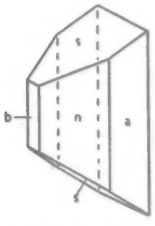

FIGURE 2 – *Struvite.*

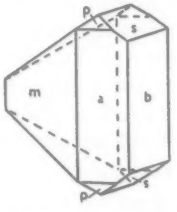

FIGURE 3 – *Struvite.*

by Barker and the present writer by Fedorov's method [2].

The success of these tests made an impression upon crystallographers, particularly upon Sir Henry Miers. At his suggestion, Barker went to Russia in 1908–9 to learn more of Fedorov's method; he returned with the hope of promoting it and making it more widely accessible. Fedorov presented his great crystal index, *Das Krystallreich*, which included some 10,000 substances, to the Russian Academy of Sciences in 1912, but it was not published until after his death in 1920 [6]. Barker collaborated in compiling *Das Krystallreich*, but he gradually became convinced that Fedorov's method, based as it was on theories of crystal structure and involving lengthy and complicated calculations, was too complex for general use. He therefore began to work out a simpler method, based, not on structure, but purely on geometrical form, and necessitating fewer calculations. He succeeded in devising a set of simple rules to be applied in choosing the classification angles for an index, and these were published in a small work, *Systematic Crystallography* [4]. Barker intended that this work should be followed by an index of crystal angles, a project in which he was encouraged by Lord Rutherford and Sir Henry Miers. The date

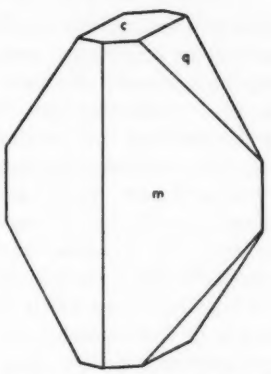

FIGURE 4 – *Acecaffin (author's position).*

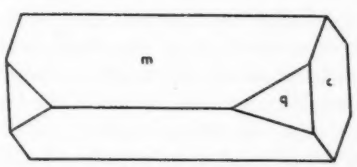

FIGURE 5 – *Acecaffin (Barker's position).*

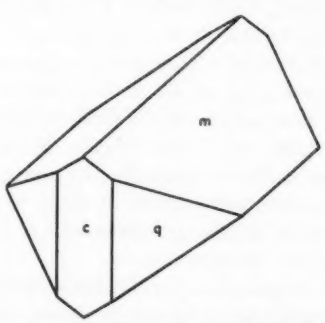

FIGURE 6 – *Acecaffin (another position).*

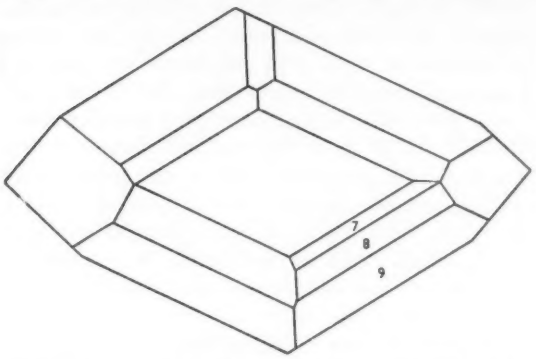

FIGURE 7 – *Topaz. Terminating faces of natural crystal.*

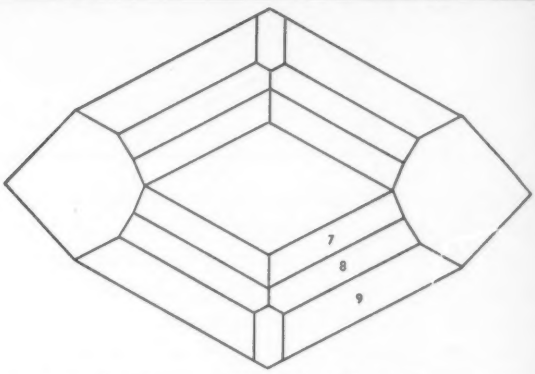

FIGURE 8 – *Topaz. Terminating faces of same crystal ideally developed.*

fixed for the start of work on the index was 1st May, 1931, but Barker died suddenly a fortnight earlier.

The possibility of compiling the Barker index after the death of its originator, and without his direction, was immediately discussed at Oxford by a number of crystallographers, and they decided to test the method independently. At the end of a year, they unanimously concluded that the method was workable, and it was decided to proceed with the preparation of the index.

After some years, the compilation of the index was held to be sufficiently far advanced to offer material for a searching test of its usefulness for the identification of compounds. An earlier test set by the present writer had been successfully carried out by Barker, and was described by him [4], but this was of limited value because Barker was exceptionally familiar with the work and because the number of substances that could then be tested was comparatively small. It was decided to carry out the new test in two of the less simple crystal systems, the orthorhombic and the monoclinic. A list of some 1230 substances which were ready for insertion in the index was sent to Dr G. M. Bennett, Government Chemist (then professor of chemistry at King's College, London), who had offered to collaborate in the test. From the list he selected 16 substances which he sent, numbered but unnamed, to Oxford [7]. Fifteen of the sixteen were successfully identified. It proved impossible to measure the remaining one as the faces were not sufficiently good to give even fair reflections on the goniometer. A list of the substances sent is given below.

It will be seen that many of these substances have a complicated chemical composition, and would be difficult to identify by other means, especially if, as was the case, only one or two small crystals were available for examination. The time taken to identify each compound varied from thirty minutes for the easier crystals to four hours for the most difficult.

List of compounds identified in a test of the Barker index

1. Ethyl-2:4-dinitrophenyl-aniline.
2. Methylanilide of benzene sulphonic acid.
3. Benzene-azo-β-naphthyl benzoate.
4. Tribenzylamine.
5. Phenyl benzoate.
6. 1-Phenyl-3-methyl-4-benzylidene-pyrazolone.
7. Methylanilide of *p*-toluene sulphonic acid.
8. Sodium nitroprusside (dihydrate).
9. Potassium sulphate.
10. Sulphur.
11. (Unmeasurable.)
12. Ammonium sulphate.
13. Eugenol benzoate.
14. Potassium nitrate.
15. Potassium dihydrogen orthophosphate.
16. Topaz.

By means of the index, F. A. Bannister and M. H. Hey were able to identify some crystals found by the Scotia Expedition in oceanic bottom samples from the Weddell Sea [8]. Several of the crystals, which varied in size from 0·2 × 0·1 mm to 0·3 × 0·15 mm, were successfully measured, and the Barker classification angles were determined. The tetragonal symmetry of the crystals was confirmed by their optics and by Laue photographs. From a table of tetragonal substances, compiled by Hey according to Barker's method, the salt was identified as hydrated calcium oxalate.

Identification in the ordinary way, by means of chemical analysis, was in this case out of the question.

The first volume of the index has now been completed [9]. It contains the classification angles of 3000 compounds belonging to the tetragonal, hexagonal, trigonal, and orthorhombic systems.

IDENTIFICATION OF AN UNKNOWN SUBSTANCE

In order to show what is involved in the use of the Barker index, a description will be given of the processes necessary for the identification of a crystal of an unknown substance. The description will be confined to the practical problem, and no account will be taken of the underlying principles. Possible complications will also be ignored, but it should not, on that account, be thought that they cannot be dealt with.

The most convenient type of instrument to use in the identification is a two-circle goniometer; such an instrument was used exclusively by both Fedorov and Barker. Hitherto the Goldschmidt two-circle goniometer has been best known. This apparatus is fitted with a telescope and collimator and two divided circles—the vertical circle (V) and the horizontal circle (H)—at right-angles to one another. The crystal is mounted with a little wax on a holder which fits into a socket on the goniometer head; it is so rotated on the goniometer that each face in turn is brought to the reflection position. Light from the collimator falls on the crystal face and is reflected through the telescope, where the image of the illuminated collimator slit is produced; this image is set as exactly as possible on the cross-wires of the telescope and readings are taken of the position on the two circles. From the V reading is obtained the angle corresponding to geographical longitude; the H reading yields the angle corresponding to the geographical latitude. A two-circle goniometer is now being made in Britain, but if a two-circle instrument is not available, the measurement of the crystal can be made with a one-circle goniometer. This is more laborious both as regards measurement (since the crystal must be remounted after the measurement of each zone) and in the subsequent making of a map or projection.

The first step in identifying a crystal is to make a freehand sketch of it so that its faces may be recognized on the goniometer during measurement. Each face is given a number, which appears in the table of measurements and afterwards in the map, or projection, of the crystal. In making his sketch the observer will note that the faces fall into a few zones, or sets of faces with parallel edges. Next, the crystal is mounted and adjusted on the goniometer, so that the axis of one of the zones is parallel to one of the goniometer axes; the V and H readings are then taken for each face and recorded.

For the sake of clarity, a specific case will now be described, and it will be assumed that the measurements obtained are those recorded in table I. Column 1 gives the number which was assigned to the crystal face in the freehand sketch. Column 2 indicates by a Greek letter the quality, whether good, bad, or indifferent, of the reflection of that particular face. In column 3, the indices of the faces are given; these indicate the relative

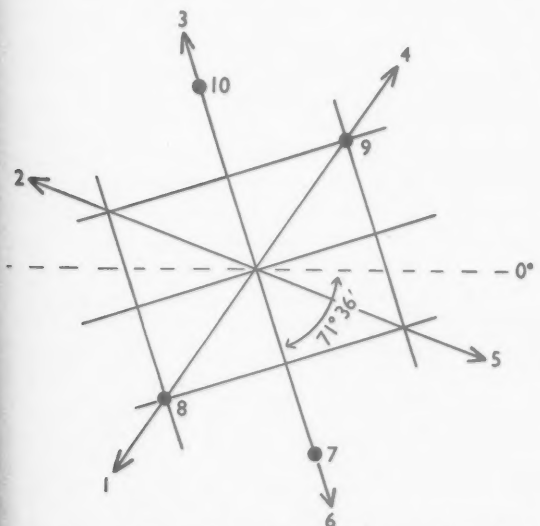

FIGURE 9 – *Gnomonic projection before φ is determined.*

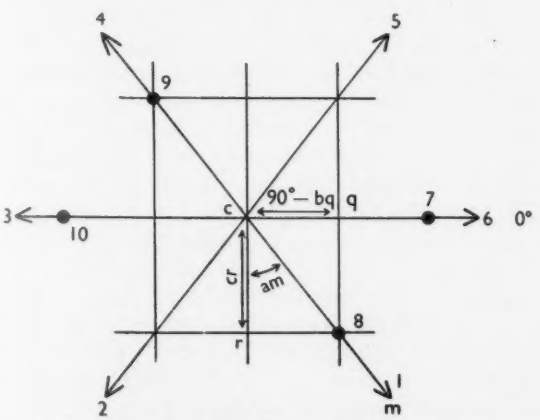

FIGURE 10 – *Gnomonic projection, φ determined.*

TABLE I

1	2	3	4	5	6	7
No. of face	*Reflection*	*Indices*	*V* (*Vertical circle reading*)	φ (= *V* − 71° 36′)	*H* (*Horizontal circle reading*)	ρ (= *H* − 10°)
1	β	m(110)	123° 39′	52° 3′	100° 0′	90° 0′
2	δ	m(1$\bar{1}$0)	199° 30′	127° 54′	100° 32′	90° 32′
3	γ	b(0$\bar{1}$0)	251° 23′	179° 47′	100° 45′	90° 45′
4	β	m($\bar{1}\bar{1}$0)	304° 2′	232° 26′	99° 55′	89° 55′
5	β	m($\bar{1}$10)	19° 47′	308° 11′	99° 52′	89° 52′
6	δ	b(010)	71° 32′	359° 56′	99° 25′	89° 25′
7	β	k(021)	71° 58′	0° 22′	46° 10′	36° 10′
8	γ	o(111)	124° 27′	52° 51′	41° 4′	31° 4′
10	β	k(0$\bar{2}$1)	251° 15′	179° 39′	46° 36′	36° 36′
9	δ[1]	o($\bar{1}\bar{1}$1)	304° 41′	233° 5′	40° 34′	30° 34′

[1] Approximate.
(Dimensions of crystal 2 × 1 × 1 mm.)

TABLE II

System: Orthorhombic Symmetry: 222
Angles: *cr* = 25° 20′, am = 37° 54′, bq = 69° 46′
Forms: m(110), b(010), k(021), o(111)

	cr	am	bq	Difference *cr*	Difference am	Difference bq
1-Naphthylamine-2-sulphonic acid ..	24° 39′	38° 27′	69° 59′	41′	33′	13′
α-Methyl glucoside	25° 6′	37° 29′	70° 14′	14′	25′	28′
Cinchonine hydriodide methylalcoholate ..	25° 8′	38° 45′	69° 22′	12′	51′	24′
Diammonium oxalate	25° 22′	37° 57′	69° 42′	2′	3′	4′
Laserpitin	25° 28′	36° 58′	70° 16′	8′	56′	30′
1:8-Dinitronaphthalene	25° 34′	36° 57′	70° 12′	14′	57′	26′
bis-Tripropylammonium platinum hexachloride	25° 47′	37° 13′	69° 52′	27′	41′	6′
Trisodium citrate pentahydrate	25° 55′	38° 51′	68° 37′	35′	57′	1° 9′

inclinations of a face to axes of reference. The readings on the vertical and horizontal circles of the goniometer are given in columns 4 and 6, and from them a projection is made (see figure 9). The two most convenient types of projection are the stereographic and gnomonic; only the latter will be considered here. In the gnomonic projection the crystal is imagined as placed at the centre of a sphere, so that the normal to each face cuts the sphere at a given point. These normals must be imagined as extended until they cut a plane tangential to the north pole of the sphere. This plane is that of the gnomonic projection, and with the two-circle goniometer it is parallel to the plane of the vertical circle. Each face of the crystal is represented on the projection by a small dot, with the exception of the prism faces, which lie in the plane of the projection and are indicated by arrows.

The V and H readings obtained for the several faces require some adjustment before the final gnomonic projection can be made, to allow for the original settings of the two scales. The corrected V and H readings are generally designated φ and ρ. Figure 10 shows the final projection made, using these φ and ρ values, so that the crystal appears in the standard position with an axis at zero longitude. The practised crystallographer, however, does not find it necessary to make two projections.

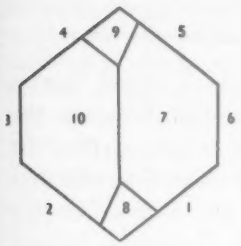

FIGURE 11 – *Orthogonal drawing of ammonium oxalate.*

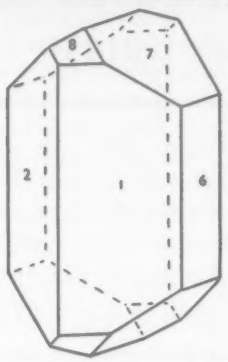

FIGURE 12 – *Perspective drawing of ammonium oxalate.*

The Barker rules are now applied. The most important rule, applicable to all the crystal systems, is contained in the 'principle of simplest indices,' that is to say, the choice of indices involving, if possible, only the integers 0 and 1. Further, as shown in figure 10, there are three classification angles for the orthorhombic system, *cr*, am, bq, and the angle am must be less than 45° and nearer to 45° than *cr* or bq. The main classification angle for orthorhombic compounds is *cr*, and compounds are listed according to this angle. The angles found for the unknown crystal which we are assuming to be under investigation are as follows:

$cr = 25° 20'$, $\quad am = 37° 54'$, $\quad bq = 69° 46'$.

Having obtained these angles, the orthorhombic classification-angle table in the index is consulted; the values of the *cr* angles from 24° 39′ to 25° 55′ are examined to allow for possible variations due to imperfections in the crystal. There are sixty-one entries between these limits, and the second classification angle must now be taken into consideration. The value of the latter cuts the list (see Table II) of possible compounds to eight, and the close agreement in angle between those of the unknown crystal and of diammonium oxalate in the list strikes the eye at once. The next step is to study the form-development of diammonium oxalate in the descriptive part of the index; this is found to be the same as that of the specimen and the identity of the compound as diammonium oxalate is established. Figure 11 is a drawing made looking down from directly above; figure 12 is a perspective drawing. The identification of this particular substance took 1½ hours.

In certain other cases of identification, it may be necessary to consult the descriptive part of the index for any one of the other simple physical properties, such as colour, cleavage, melting-point, density, or optical properties; this course was strongly recommended by Barker for confirming the determination.

It has been shown in some detail that the Barker method can be of practical value to the chemist, and it may be added that it has some peculiar advantages over other methods of identifying chemical substances. For example, the amount of material required is very small, since a crystal measuring no more than half a millimetre in any direction can be classified, and the material is left intact at the end of the measurement. Yet another advantage is that a complex compound can be identified as quickly as a simple one, and in far less time than a chemical analysis would take.

It is a pleasure to record the assistance offered from many quarters in the crisis which followed Dr Barker's untimely death so shortly before work on the index was due to begin. With the kind permission of the late Professor H. L. Bowman, those engaged in compiling the index made their headquarters in the mineralogical department of the University Museum at Oxford. On Professor Bowman's retirement in 1941 these facilities were continued by Mr R. C. Spiller and Mr H. M. Powell. Since 1948, the working headquarters have been in the department of geology and mineralogy, by kind permission of Professor J. A. Douglas and of his successor, Professor L. R. Wager.

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The polyhedral diseases of insects

KENNETH M. SMITH

Although their serious investigation is of very recent date, the viruses which attack insects have already proved to be most interesting. Particularly so is the association between the virus particles themselves and the extremely tiny polyhedral crystals which form within the bodies of infected caterpillars. These crystals, which withstand drying, are extremely efficient carriers of the disease, and attempts have been made to use them for practical ends—for example, in attacking the spruce budworm, which is a serious pest in Canadian forests.

In 1892 a Russian botanist, Iwanowsky, was investigating a disease of the tobacco plant, known as tobacco mosaic, and during his experiments he demonstrated that it was caused by an agent so small that it could pass through the pores of a bacteria-proof filter-candle. This discovery of the filterable viruses opened the door to a kingdom probably as large as that revealed in the seventeenth century by van Leeuwenhoek's discovery of his 'little animals.' The two discoveries are, however, not quite comparable. By means of the microscope—even the primitive instruments of van Leeuwenhoek—it was possible to see and describe bacteria and other inhabitants of the new world of microbiology. No optical microscope can reveal the viruses, because, with very few exceptions, they are beyond the resolving power of microscopes using visible light. The invention of the electron microscope and the development of the ultracentrifuge have, however, transformed the situation, and it is possible with modern techniques to see and to photograph even the smallest viruses.

Viruses attack all kinds of living organisms, from bacteria to man himself. Those which have been most closely studied are, apart from those attacking the higher animals, the plant viruses and the bacterial viruses; the latter used to be called bacteriophages. There is, however, a large group of viruses which attack insects, and these, for some reason, have not received much attention until very recent times. This is rather curious, because many of them are of very great interest, particularly as regards the extraordinary changes which take place inside the body of the infected insect. The resulting diseases are called polyhedral diseases because of the development in the body of the insect of huge numbers of many-sided crystals, some of which can be seen in figures 2, 4, and 10.

TYPES OF INSECTS ATTACKED BY VIRUSES

Virus diseases of the polyhedral type have been recorded from various kinds of insects, but mainly from those belonging to the *Hymenoptera* (ants, bees, and wasps) and the *Lepidoptera* (butterflies and moths). By far the greater number has been recorded from the *Lepidoptera*, though no doubt with further study other groups will be found to be susceptible. An interesting feature about polyhedral insect viruses is that they attack only the larval stages, the adult insects apparently being immune.

Several of these virus diseases affecting caterpillars have been known for a number of years; they must, however, represent only a fraction of the viruses which exist. Indeed, experience at Cambridge has shown that if caterpillars are bred on a large scale for some time, a virus disease always appears eventually. This has proved to be so with five species of tiger-moth larvae, four species of the so-called giant tropical silk-moths (figure 1), and the currant-moth (*Abraxas grossulariata*). None of these viruses had been previously described. A possible explanation of the sudden appearance of a virus in a group of apparently healthy caterpillars will be discussed later.

Two of the best-known polyhedral diseases of caterpillars are those attacking the silkworm (*Bombyx mori*) and the nun-moth (*Lymantria monacha*). The first of these diseases is usually known as 'jaundice', because of the yellow colour assumed by the infected silkworms. The Germans gave the second the peculiar name of *Wipfelkrankheit*, or tree-top disease. This was because towards the end of the last century a tremendous epidemic broke out among the great populations of nun-moth larvae which were destroying much of the spruce forests of central Europe. The infected caterpillars tended to migrate to the tops of the trees, where they died but remained hanging, attached by

their abdominal feet. Such dead caterpillars are merely limp sacks half-full of polyhedral bodies. It has been suggested that this wholesale migration to the tree-tops might be connected with partial suffocation due to the pressure of the polyhedral bodies on the fine tracheal breathing tubes. On this assumption the caterpillars make for the tops of the trees, where there are more air currents. The rapid disintegration of the internal tissues is typical of the effects of these caterpillar viruses. In figure 9 may be seen a dead caterpillar of a foreign silk-moth (*A. io*) hanging characteristically by its abdominal feet.

HOW THE POLYHEDRAL VIRUSES SPREAD

It is certain that the caterpillar viruses are very highly infectious. The polyhedral bodies are not the virus particles themselves, as was thought at one time, but they do contain virus. They are extremely stable, and can be dried and still retain infective virus within them. When they enter the gut of a susceptible caterpillar, they are dissolved by the action of the alkaline secretions, and the virus particles are liberated. The polyhedra act, so to speak, as an extremely efficient kind of parcel-post for the distribution of the disease. One method, therefore, by which caterpillars can become infected is by ingesting the polyhedra while eating leaves contaminated by infected caterpillars. The efficiency of this method of distribution seems, however, to vary with the species of caterpillar, and hence also with the virus, since they are extremely specific in their action. Thus it is easy to infect the larva of the currant-moth by moistening the mouth-parts with a suspension of polyhedra, but less easy to infect some other species in the same manner.

The contamination of the food materials and surroundings by polyhedra is ensured by the symptoms induced by the disease. In some species the infected caterpillar excretes large quantities of fluid containing polyhedra (see figures 6 and 10); the faeces also are infectious. In the last stages of the disease the caterpillar is, as already pointed out, converted into a mere sack filled with polyhedral bodies. The skins of such caterpillars rupture very easily, liberating millions of polyhedra, which, being able to withstand drying, spread infection far and wide. Another and very important method of propagation of polyhedral diseases is by the passage of the virus from parent to offspring; this is a phenomenon which is comparatively rare in the virus diseases of plants and the higher animals.

A description of a polyhedral disease as it occurs in the larvae of the oak silk-moth (*Telea polyphemus*, figure 1) will serve to illustrate some of these points. When a half-grown caterpillar of this species is artificially infected with its specific polyhedral virus, either by ingestion or inoculation, the insect becomes sluggish and ceases to grow, although it may for a time continue to feed. Frequently drops of fluid, at first colourless but later turning black, exude from the body of the animal (figure 6). If such drops are examined under the oil-immersion lens of the optical microscope they will be found to contain large numbers of polyhedral bodies (figure 10). It occasionally happens that larvae becoming infected when nearing maturity complete their larval life, make their cocoon, and may even pupate. If, under these conditions, the cocoon is cut open the dead larva or pupa is found full of polyhedral bodies (figure 7). These remarks apply to the caterpillar which is actively diseased. Sometimes, however, it seems clear that the virus may be present in a latent condition within the caterpillar. The evidence for this is as follows. Apparently healthy caterpillars of the oak silk-moth pupated and gave rise to adult moths. From these moths a number of fertile eggs were obtained. Of the caterpillars arising from these eggs a percentage died of polyhedral disease, the age of the caterpillars varying from fourteen days to less than forty-eight hours. Examination of the caterpillars which died within forty-eight hours of emerging from the egg showed that they contained large numbers of polyhedral bodies. This is interesting, because it indicates that the virus must have been inside the developing larva within the egg, and not merely outside on the shell. It is hardly feasible that so many polyhedra would have developed within forty-eight hours if infection had been derived from the outside of the egg at the moment of emergence of the young larva.

Similarly, some hundreds of larvae of the garden tiger-moth (*Arctia caja*) were bred in the laboratory in a room where no tiger-moth larvae had ever previously been kept. The caterpillars, which were perfectly healthy, were bred continuously through four generations without going through a diapause (resting period). In the fifth generation, a polyhedral disease developed and wiped out the entire stock of caterpillars. It seems clear, therefore, that these polyhedral viruses must be capable of lying latent within the body of a susceptible caterpillar, being passed from one generation to another until, under some stimulus, the nature of

which is at present unknown, the virus begins active multiplication and gives rise to the disease. It is possible that careful examination of the tissues of apparently normal caterpillars by means of the electron microscope may yield further knowledge of these latent infections.

The claim has been made on more than one occasion that it is possible to produce virus in silkworms *de novo* by feeding the caterpillars on certain chemicals, and it seems true enough that under some circumstances silkworms, when fed on various chemicals, develop a polyhedral disease. Yet a more likely explanation seems to be that the virus is already present in the animal in a latent or quiescent form, and that the chemical acts as the trigger which sets the virus multiplying and thus causes the disease to develop.

CHANGES TAKING PLACE INSIDE THE DISEASED CATERPILLARS

The polyhedral diseases of insects are sometimes referred to as nuclear diseases because the pathological changes seem to start inside the cell nucleus. Whether all polyhedral diseases begin to develop inside the cell nucleus is not certain; perhaps in some cases the focus of multiplication is in the cell cytoplasm. At all events there is no question but that at some stage in the polyhedral disease these curious many-sided crystals begin to form inside the nuclei of susceptible cells. In figure 2 is shown a photomicrograph, taken with the optical microscope, of a section through a caterpillar of the currant-moth infected with a polyhedral virus disease. The apparent honeycomb structure of the enormously enlarged nuclei is due to the fact that they are packed with polyhedral bodies. A similar state of affairs is illustrated in figure 4, which shows a single cell nucleus from the larva of the common clothes-moth (*Tineola bisselliella*) infected with a polyhedral disease. Judging by the expansion caused by the pressure of the polyhedral bodies contained within it, the nuclear membrane must be extremely elastic. However, the nucleus eventually bursts, liberating the crystals into the surrounding cytoplasm. As the disease progresses, the cells disintegrate, until the caterpillar assumes the condition shown in figure 9.

THE NATURE OF THE POLYHEDRAL BODIES

The relationship between the polyhedral bodies and the virus itself has long been sought. For a time they were thought to be some kind of organism causing the disease, and were given names like *Crystalloplasma polyedricum* and *Chlamydozoon prowazeki*. It was not until quite recently, however, that it was shown that these bodies, which appear to be genuine crystals, are not themselves the infective agents but contain some virus inside them [1, 2].

If a polyhedral body is dissolved in weak sodium carbonate solution and the process followed under the high power of the optical microscope, using dark-ground illumination, an interesting phenomenon can be observed. Each polyhedral body is enveloped in a kind of skin or membrane, and, as the substance of the crystal dissolves, numbers of highly refractive dots can be seen vibrating violently inside the membrane; occasionally one or two pass right out of the membrane and disappear. These dots are the virus particles themselves, which are too small to be resolved by the optical microscope and so appear in the dark field as bright points of light driven about inside the enclosing membrane by Brownian movement.

A much clearer picture of what happens when the polyhedral body is dissolved can be obtained by means of the electron miscroscope, using a magnification of about ten thousand. Figure 5 is an electron micrograph, taken by Dr R. W. G. Wyckoff; it shows, collapsed, the membrane which enclosed the polyhedral body before it was dissolved in weak alkali. The rod-shaped virus particles which have been liberated can be clearly seen. This particular polyhedral body came from an infected caterpillar of the scarlet tiger-moth (*Panaxia dominula*), and well-defined virus rods are always present in this disease. Although many of the polyhedral viruses of insects seem to consist of rod-shaped particles [1, 2], it does not follow that all viruses of this type are rod-shaped. Indeed, there is good evidence that some of the polyhedral viruses are spherical [3], while in other polyhedral diseases no virus particles have as yet been seen.

It will be realized from this brief description of the polyhedral bodies that there is still much to be learnt about their function. We know that they are protein crystals, but of a protein different from that of the virus particles themselves, and that they contain, in some diseases, about 3–5 per cent. of virus. But what is the purpose of the crystals, and why is each crystal enclosed in a membrane? Again, how do the virus particles get into the crystal? Are they occluded during the growth of the crystal, or do they actually form inside it? At the moment we have no answers to these questions, but it seems unlikely that any growth

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FIGURE 1 – *Female oak silk-moth* (T. polyphemus). (*Slightly reduced.*)

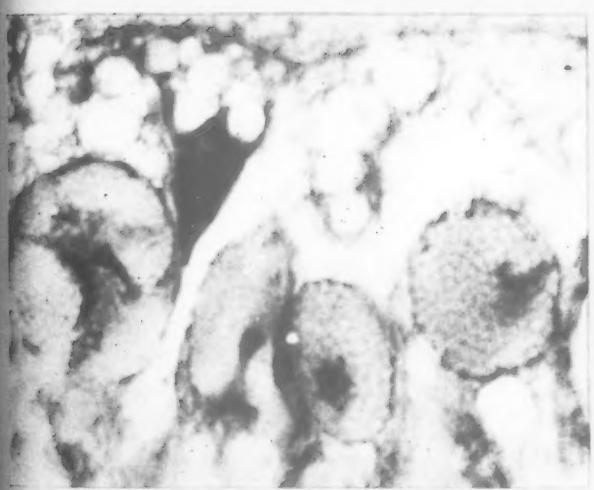

FIGURE 2 – *Transverse section through a caterpillar of the currant-moth* (Abraxas grossulariata) *infected with polyhedral disease. Note the cell nuclei packed with polyhedra and enormously distended.* (× *c.* 1200)

FIGURE 3 – *Caterpillars of the common clothes-moth* (T. bisselliella) *killed by a polyhedral disease. A few normal larvae, pale in colour, can be seen.*

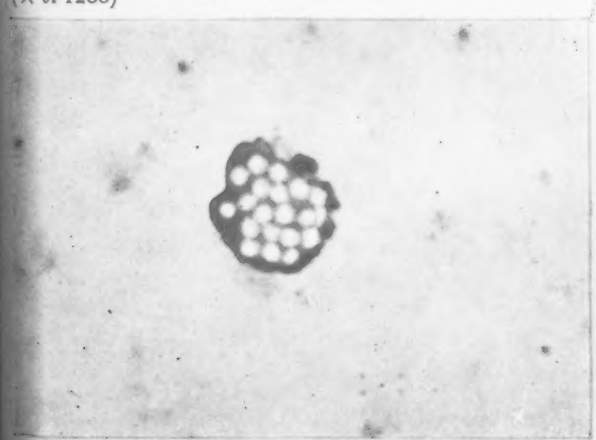

FIGURE 4 – *A cell nucleus from one of the dead larvae seen in figure* 3. *Note the polyhedral bodies.* (× *c.* 1500)

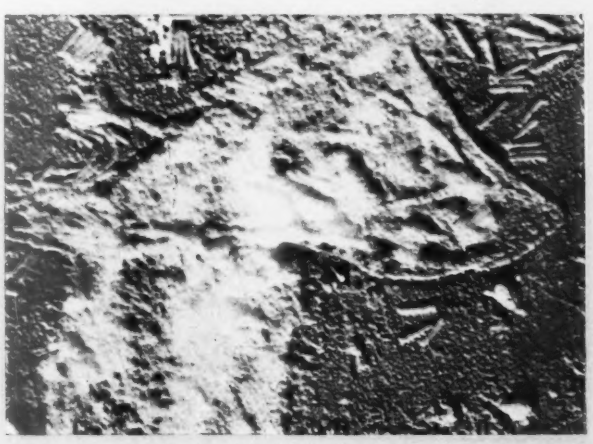

FIGURE 5 – *A single polyhedral body from the caterpillar of the scarlet tiger-moth* (Panaxia dominula). *The crystal has been dissolved in weak alkali, leaving the enclosing membrane and liberating the virus rods.* (× 10,500)

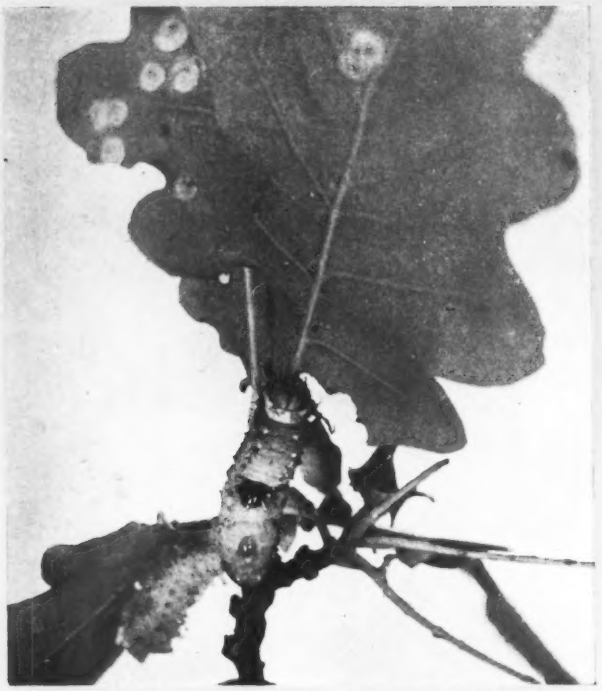

FIGURE 6 – *Two caterpillars of the oak silk-moth infected with a polyhedral virus disease. Note fluid oozing from the dorsal surface of caterpillar in centre.* (*Slightly reduced.*)

FIGURE 7 – *Infected caterpillar of the oak silk-moth which has failed to pupate; cocoon opened to show dead larva full of polyhedral bodies.*

FIGURE 8 – *Healthy caterpillar of the oak silk-moth.* (*Slightly enlarged.*)

FIGURE 9 – *A caterpillar of the bull's eye moth* (A. io) *dead from polyhedral disease. Note the characteristic appearance of the dead larva—a sack full of polyhedra, hanging by one of the abdominal feet.*

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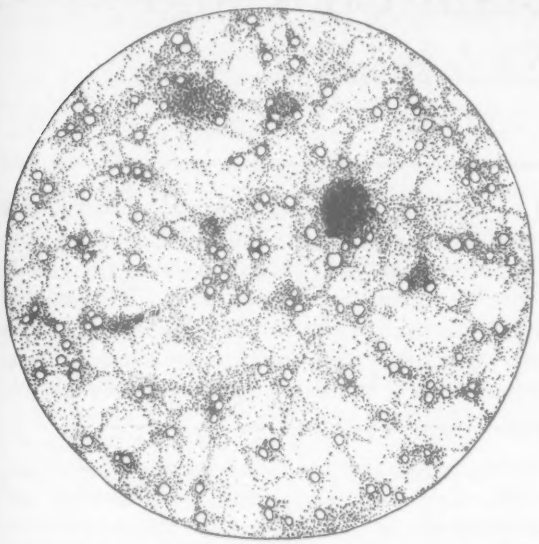

FIGURE 10 – *Fluid from the infected caterpillar shown in figure* 6 *seen under the microscope. Note the large numbers of crystal-like polyhedral bodies.* (× *c.* 750)

could take place inside the actual crystal. Nor does it seem possible that such large numbers of virus rods as occur in some instances could be accidentally occluded during crystal formation. It may be that the formation of the polyhedra is a process analogous to the formation of a pearl in the oyster, and that the crystal is formed in response to the stimulation of the virus rods. It should be realized, however, that polyhedral bodies frequently occur which do not contain any virus rods, even in those diseases where rods are present.

In a study by Dr Wyckoff and the present writer it has proved impossible to demonstrate the presence of any virus in the polyhedra of some diseases. This is true, for example, of the disease attacking the common clothes-moth (*Tineola bisselliella*). Yet the polyhedra are intensely infectious and the larvae are killed by ingesting them with their food (figure 3). It may be, of course, that a new technique is necessary to demonstrate the presence of some of these viruses, but it does not seem to be a question of the virus particles being missed in the electron microscope by reason of their small size.

POSSIBLE USE OF VIRUS DISEASES TO CONTROL INSECT PESTS

We have already mentioned the occurrence of a great epidemic of polyhedral disease among the nun-moth caterpillars in central Europe. Such naturally occurring epidemics have suggested the possibility of stimulating similar virus epidemics among other insect pests by artificial means. Several attempts on these lines are being made at the present time. In Canada, where the spruce budworm is a serious threat to the spruce forests, a virus has been obtained which attacks this insect, and a scheme is afoot to use it to keep down the numbers of the pest.

In California [4] some experiments have already been made, using a polyhedral virus against the caterpillars of the alfalfa (lucerne) butterfly. Huge quantities of infective polyhedra were obtained, either by breeding very numerous caterpillars and infecting them with the virus, or by collecting in the field large numbers of caterpillars already infected. It was found that application of a virus suspension containing 5 million polyhedra per ml at the rate of 23 litres per acre was adequate to ensure infection of a field population of larvae, and to reduce its numbers below an economically serious level, at least under the conditions then obtaining in the northern San Joaquin valley. Application by means of a small aeroplane was found to be the most convenient method of treating large fields with a virus suspension. Ground equipment would be more suitable for application to small fields.

Figure 3 shows the result of disseminating polyhedral bodies among a culture of the caterpillars of the clothes-moth. This virus is very efficacious in destroying the larvae of the clothes-moth in small enclosed spaces such as trunks, wardrobes, chests-of-drawers, or cupboards, but its efficiency on a large scale has not yet been properly tested. Much work remains to be done on the factors governing the spread of the disease on a large scale.

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A link with Captain Cook and H.M.S. *Endeavour*

H. ALAN LLOYD

In the past, the difficulties of navigation and of making exact astronomical observations were very largely due to the lack of exact and reliable chronometers. This article shows that less than two centuries ago several major scientific observations in various parts of the world were—surprisingly enough—dependent upon the use of one particular clock. This clock, made for the Royal Society by John Shelton, travelled between London and places as far afield as St Helena, Barbados, Pennsylvania, and the Arctic, surviving among many other vicissitudes the hazards of shipwreck. Today it is still an excellent timekeeper.

In appraising the efforts of former generations of scientists one is apt to forget the limitations placed on them in the execution of their work by their limited apparatus and equipment. Thus, today, it is perhaps difficult to realize that when the *Endeavour* sailed in 1768, carrying a party of scientific workers to observe the transit of Venus in the South Pacific, the best timekeeping instrument available was a long-case clock with a pendulum of approximately 39 inches, beating seconds. The chronometer, as we know it today, was just being born; at that date there was in existence only one spring-driven timepiece sufficiently accurate to determine longitude at sea. This was John Harrison's No. 4, which had been tested on two voyages, one to Jamaica in 1761 and the other to Barbados in 1764. It was on Cook's second voyage in 1776 that he carried, in the *Resolution*, Larcum Kendall's copy of Harrison's No. 4, which won from him such praise. Larcum Kendall also made the chronometer carried by Bligh in the *Bounty*.

Thus it came about that for the voyage of 1768, Cook had still to rely on dead-reckoning to determine his longitude. When the expedition landed, a long-case clock with a gridiron pendulum was the most reliable timekeeper available. The gridiron pendulum also was an invention of John Harrison; he used it first in his No. 1, which was tested in 1735. The clock used by Cook was one by John Shelton and was lent by the Royal Society, which organized the expedition; it is still in the Society's possession and is in continuous use in the room of one of the officers.

The history of this clock began at a meeting of the council of the Royal Society held on 2nd July, 1760. Preparations were then being made for sending two expeditions to observe the transit of Venus across the Sun's disk on 5th June, 1761. This was the first such transit to occur since 4th December, 1639, when Jeremiah Horrox had succeeded for the first time in observing this rare occurrence. A considerable number of expeditions were then being organized by governments and academies for observations of the transit, with a view to an improved determination of the Sun's distance. It was resolved to buy for £20 'a clock with a pendulum adjusted so as to obviate the variable effects of heat and cold for the observations at the Island of St Helena.' On 14th July Nevil Maskelyne, the Astronomer Royal, was chosen to lead the expedition, with Charles Mason as his assistant; at this meeting it was resolved 'to add £10.10.0 to the price of the clock for a more complete timepiece.'

At about the same time, a second clock was ordered from Mr John Ellicott, F.R.S., a noted clockmaker. Ellicott's clock has nothing to do with the journey of the *Endeavour*, but is mentioned here because, as two expeditions were being fitted out at the same time, the statement that Ellicott's clock was sent on one of them leaves the inference that the Shelton clock was sent on the other.

On 27th December, 1760, Maskelyne and Waddington signed for, and promised to return to the Royal Society, *inter alia* . . . 'a clock with a gridiron pendulum.' On the same day Charles Mason, who had now been appointed to lead a similar expedition to Bencoolen, and Jeremiah Dixon, his assistant, signed for 'a clock by Mr Ellicott.'

On his return from St Helena, Maskelyne, writing on 12th January, 1762, refers to the various experiments that had already been carried out by others to determine the force of gravity in different parts of the earth by measuring the length of the seconds pendulum, and states that he

took the opportunity of making similar observations on the occasion of his visit to St Helena; 'the Royal Society furnished me with an excellent clock, with a gridiron pendulum adapted to it, executed by that diligent and ingenious artist, Mr John Shelton.

'Soon after my arrival at St Helena, I set up the clock in the valley near St James' Fort. . . . The pendulum had not been taken off the clock, for carriage, but was secured to the clock case, in order to prevent it from receiving any damage. A piece of wood was secured to the back of the clock case, having a round cavity in it before, just large enough to receive the bob of the pendulum; another piece of wood, with such another cavity in it, likewise fitting the bob of the pendulum, was applied to it, on the forepart, and secured firmly to the other piece, and to the back of the clock case. Two little pieces of wood likewise kept the upper part of the pendulum in its place, from receiving any motion near the centre of suspension.

'When the pieces of wood were taken away and the pendulum thereby disengaged, the clock was fit for use: only to adjust the pendulum to the same exact length, as it was set at Greenwich, a mark had been made on the rod, where the top of the pendulum rose to; and Dr Bradley informed me of the number, which stood against the index, on the nut at the bottom of the pendulum, by screwing or unscrewing which, the bob is elevated or depressed.'

The holes in the back of the case where the clamps were fixed to the bob of the pendulum and at the base of the gridiron can be clearly seen in figure 2. The marks made on the pendulum rod before it left Greenwich are seen in figure 3.

In his report read to the Royal Society on 20th December, 1764, and 20th January, 1765, on his observations in St Helena in 1761, Maskelyne notes 'On October 28th, I took down the clock, packed it up, and sent it aboard a vessel going to the Cape of Good Hope, to return again soon, committing it to the care of Mr Jeremiah Dixon, who had observed the transit of Venus over the sun at the Cape.' (The expedition to Bencoolen, incidentally, did not materialize, for political reasons.) 'He took his passage on board the same vessel, in order to set the clock up at the Cape of Good Hope; and examine the difference of the proportion of the force of gravity, at those two places.' Mason appears to have joined Maskelyne at St Helena, as Maskelyne writes further, 'the same day Mr Mason fixed up his clock for my use. . . . This clock was made by Mr John Ellicott, F.R.S.

'I still continued, for some time, to make observations in the upper room, as before. For this I fixed up a little clock there, which may be called a journeyman clock, having a pendulum swinging seconds, which, after being well adjusted, would keep time regularly for several hours. It had only minute and seconds hands, and struck every minute exactly as the second hand came to sixty, which was very convenient for counting seconds; . . . The little clock, as well as the larger clock which I sent with Mr Dixon to the Cape of Good Hope, was made by Mr John Shelton.'

On 19th November, 1761, Waddington reports from St Helena. On the same date it is 'ordered that £35.8.0 be paid to Mr Ellicott for his regulator.' It is also 'advised that the Society's observers have gone on to the Cape of Good Hope.' On 13th May, 27th May, and 17th June, 1762, are recorded the return of the instruments from the Cape and St Helena.

In 1763 Shelton's clock is again in demand, the Society's minutes of 18th August recording that a letter had been received from Maskelyne requesting the loan of Mr Shelton's clock made for the Society. This was required for use in Barbados, whither Harrison's No. 4 was being sent on its second test in connection with his claim for the £20,000 reward offered in 1714 for solving the problem of accurate measurement of longitude. This sum was to be paid 'to anyone who should invent a practicable method of determining the longitude within ½°.'

Harrison's No. 4 had already made one journey to Jamaica, in 1761, when, after allowing for its rate of going, it was found to be 5 seconds slow, corresponding to an error of longitude of only 1¼ min. On 14th February, 1764, H.M.S. *Tartar* sailed from the Nore with Shelton's clock aboard. On this trip the error of Harrison's chronometer was only 38·4 sec in seven weeks, equal to 9·6 miles of longitude at the Equator.

On 17th October, 1765, a letter was addressed to the Society by Mason and Dixon, proposing to measure a degree of latitude and a degree of longitude in the neighbourhood of Pennsylvania. To this the Society agreed, and on 8th November, 1765, Maskelyne wrote to them to say 'As I do not find that you have a clock with you, I shall make a proposal to the Council of the Royal Society, that their clock, which I took to St Helena and the Barbadoes, may be sent you. . . . Always fix the Clock up firm and adjust the

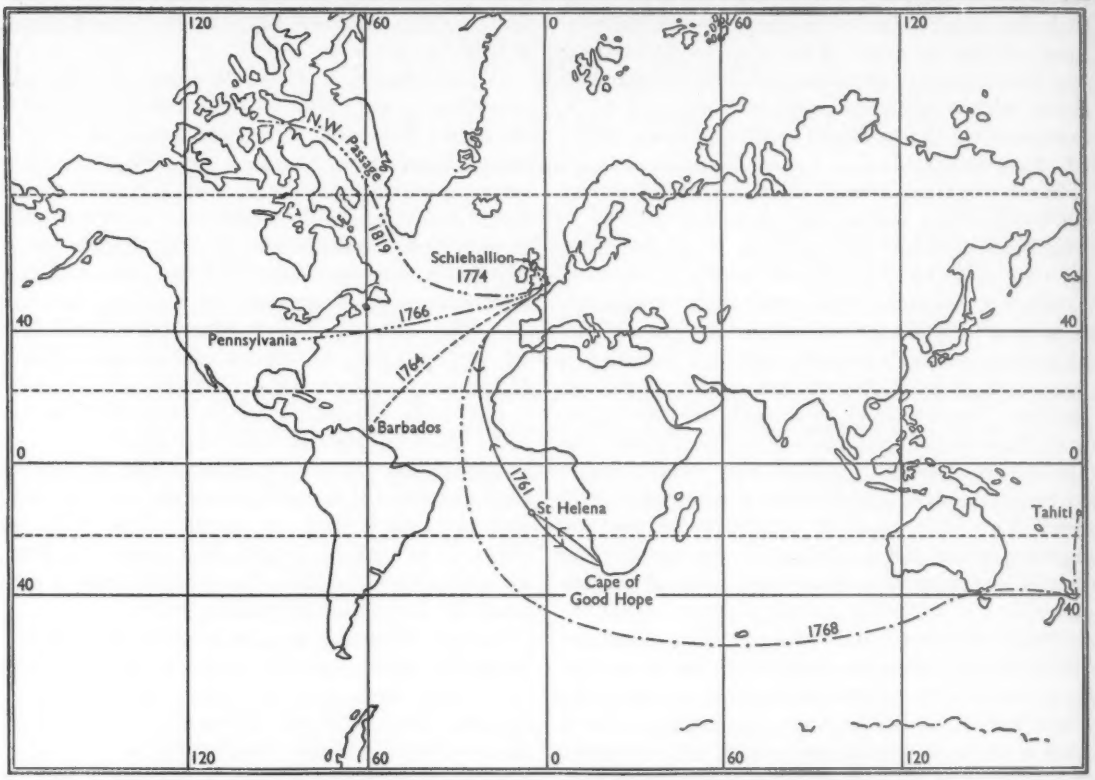

FIGURE 1 – *The journeys of John Shelton's clock*, 1761–1819. [*Diagrammatic.*] *The clock was used only on land.*

pendulum to the same length, and it will keep the same rate of going very nearly. . . .

'Should the Clock be sent you, adjust the pendulum to the Upper Scratch, No. 3 standing against the Index, which answered to sidereal time in St Helena, and keep the clock going for some days, in order to determine its rate of going. . . .'

On 14th November, 1765, Mason and Dixon were advised that the clock, together with other supplies, had been embarked on the *Ellis*, commanded by Samuel Richardson Egdon. This ship sailed in December of that year.

It would appear that the ship was wrecked, for the minutes of August 1766 record the 'supposed wreck of the ship *Ellis*, wherein were the Instruments sent to Messrs Mason and Dixon.' On 15th January, 1767, the Council ordered 'that a letter be sent Messrs Mason and Dixon . . . desiring the return of the clock that had been damaged without Delay.'

The damage to the clock appears to have been confined to a broken suspension spring. Mason and Dixon carried on with it after effecting repairs. Mason writes in his journal: '1766, December 11. The Sector was set up at Mr Harlands. . . . Here we also set up the Clock sent us by the Royal Society of London.' '1766. December 15. This day we set the pendulum of the Royal Society's Clock to the upper Scratch with Number 3 at the Index; as desired by Mr Maskelyne.' Mason and Dixon finished their work by 25th February, 1767, and the clock was taken down and packed in its case on 28th February.

In the meantime, the Society, fearing that the clock had sustained severe damage in the shipwreck, sent a letter of recall on 1st January, 1767, in order to put it right for the observation of the transit of Venus on 3rd June, 1769. This was received by Mason on 24th May, and the clock was carried by four men to Wilmington, and thence by water to Philadelphia. On 19th November, 1767, Maskelyne reported the clock safely back and going at Greenwich.

The transits of Venus occur in pairs with an interval of eight years, the intervals between the pairs being alternately 121½ years and 105½ years. In 1768 arrangements were in hand for expeditions to be sent to observe the transit of 1769.

FIGURE 2 – *The clock made by John Shelton in 1760. The total height of the case is 5 ft 7½ in. The holes in the backboard were used for the clamps which held the gridiron pendulum in position on the clock's many journeys. Note the rating nut below the pendulum bob.*

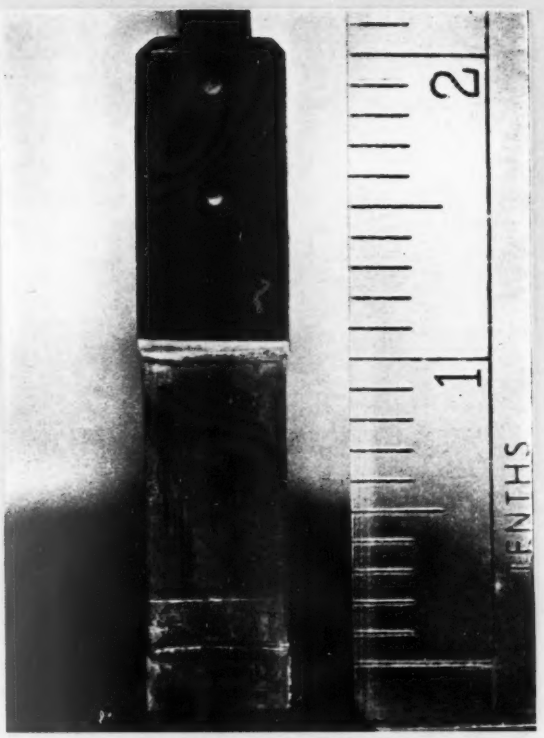

FIGURE 3 – *Marks made on the pendulum by Dr Bradley to indicate the correct position of the bob at Greenwich. The scale on the right is graduated in inches.*

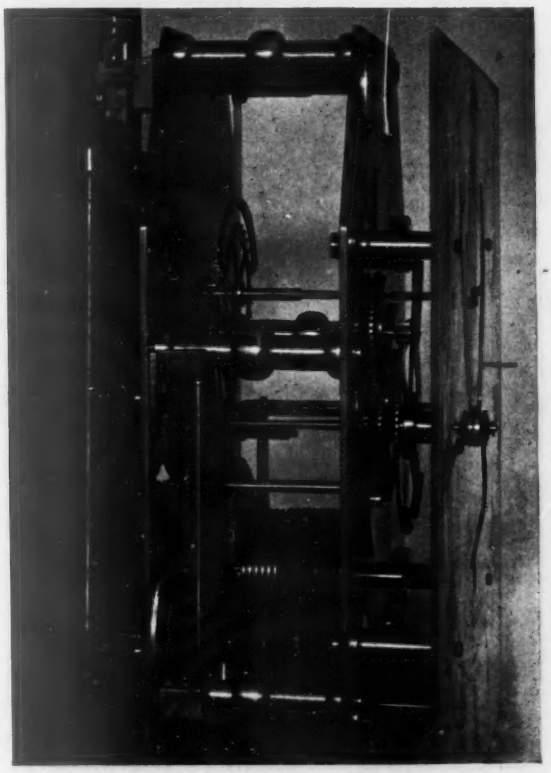

FIGURE 4 (*right*) – *Side view of the mechanism of Shelton's clock.*

The Society's minutes of 5th May, 1768, record that 'Capt Campbell having mentioned that Capt James Cook,[1] who now attended, will be appointed by the Admiralty to the Command of the vessel destined for the Observations in the Southern Latitude. . . . Mr Cook was called in and he accepted the Employment.' Among the instruments allotted were 'An astronomical clock and an alarm clock now at the Royal Observatory. . . .'

At about the same time an expedition was being organized to go to Hudson Bay. The Society's minutes of 10th March record 'Ellicott's clock to go with the Observers at Hudson Bay.'

On 23rd June, 1768, instructions were given to Cook and to Mr Charles Green to go to the newly discovered island, King George's Island (Tahiti), to observe the transit of Venus: 'begin making your observations without any loss of time, remembering to put the bob of the pendulum at the same height exactly, as it was at the Royal Observatory at Greenwich before the voyage, by means of the marks made on the pendulum for that purpose, in order to find the difference in gravity, between Greenwich and your place of Observation. . . .' On 21st July, 1768, Cook and Green signed for 'An Astronomical Clock, an Alarm Clock, A Journeyman Clock. . . .'

The results of the expedition are given in the *Philosophical Transactions* for 1771. 'At Fort Venus, Royal Bay, King George's Island, 1769, April 15th. The astronomical clock, made by Shelton and furnished with a gridiron pendulum, was set up in the middle of one end of a large tent, in a frame of wood made for the purpose at Greenwich, fixed firm and as low in the ground as the door of the clock case would admit. . . . The pendulum was adjusted to exactly the same length as it had been at Greenwich. . . . The daily rate of the clock's losing on mean time . . . is 20·8 seconds. By the first and last day's observations compared together, the clock lost 19′ 49·9″ on mean time in 57 days, which is at the rate of 20·88″ or 20·9″ per day. . . .' Maskelyne adds a note: 'The same clock, when fixed up at the Royal Observatory at Greenwich, before the voyage, with a pendulum of the same length, got a rate of 1′ 45·8″ per day, on mean time, between April 19 and July 18, 1768. Therefore the force of gravity at Greenwich is to that at King George's Island as 1000000 to 997075.'

On 27th January, 1774, the council of the Royal Society selected the mountain of Schiehallion, in Scotland, for experiments to ascertain the extent of the deflection of a plumb-line caused by the attraction of the mountain mass, and thence to determine the mean density of the Earth. On 5th May of that year Maskelyne was asked to carry out the work. He took with him the 'astronomical clock by Shelton . . . which had been provided on occasion of the observations of the transit of Venus in 1761 and 1769.'

Lastly, the much travelled clock visited the Arctic regions. Parry, in his 'Journal of a Voyage for the discovery of the North West Passage, Performed in the years 1819–20 in H.M.S. *Hecla & Griper*, under Lieutenant Wm. Ed. Parry R.N., F.R.S.,' states in the Appendix, page 164: 'Two clocks were used in these experiments, being the property of the Royal Society, and the same which accompanied Captain Cook around the World.'

It is a great tribute to the skill of John Shelton that his clock, after so many vicissitudes and buffetings, should be still going today and recording time accurately. Of Shelton himself, Mr Robinson, lately librarian to the Royal Society, notes that he was born at Clerkenwell, London, in 1702. He was apprenticed to Henry Stanbury for seven years in 1712, and when free joined the Clockmakers' Company, being admitted by the Livery on 16th July, 1766. He worked for a long time for George Graham. Other clocks by him are at Greenwich Observatory, Armagh Observatory, and the History of Science Museum at Oxford. In spite of his skill and hard work he does not appear to have prospered, for on 22nd November, 1777, the president of the Royal Society presented to the Board of Longitude a petition by John Shelton in which he represented himself, his wife, and his family as 'totally destitute and in a very helpless condition and therefore praying for relief.'

[1] The rank of Captain here given to Cook was a courtesy one, though he had commanded various sloops before this date. Actually he was commissioned as Lieutenant for the command of the *Endeavour*. He was not promoted Captain until 1775.

The clock is illustrated by permission of the Royal Society. Figures 3 and 4 are by Mr Kaye, librarian of the Royal Society.

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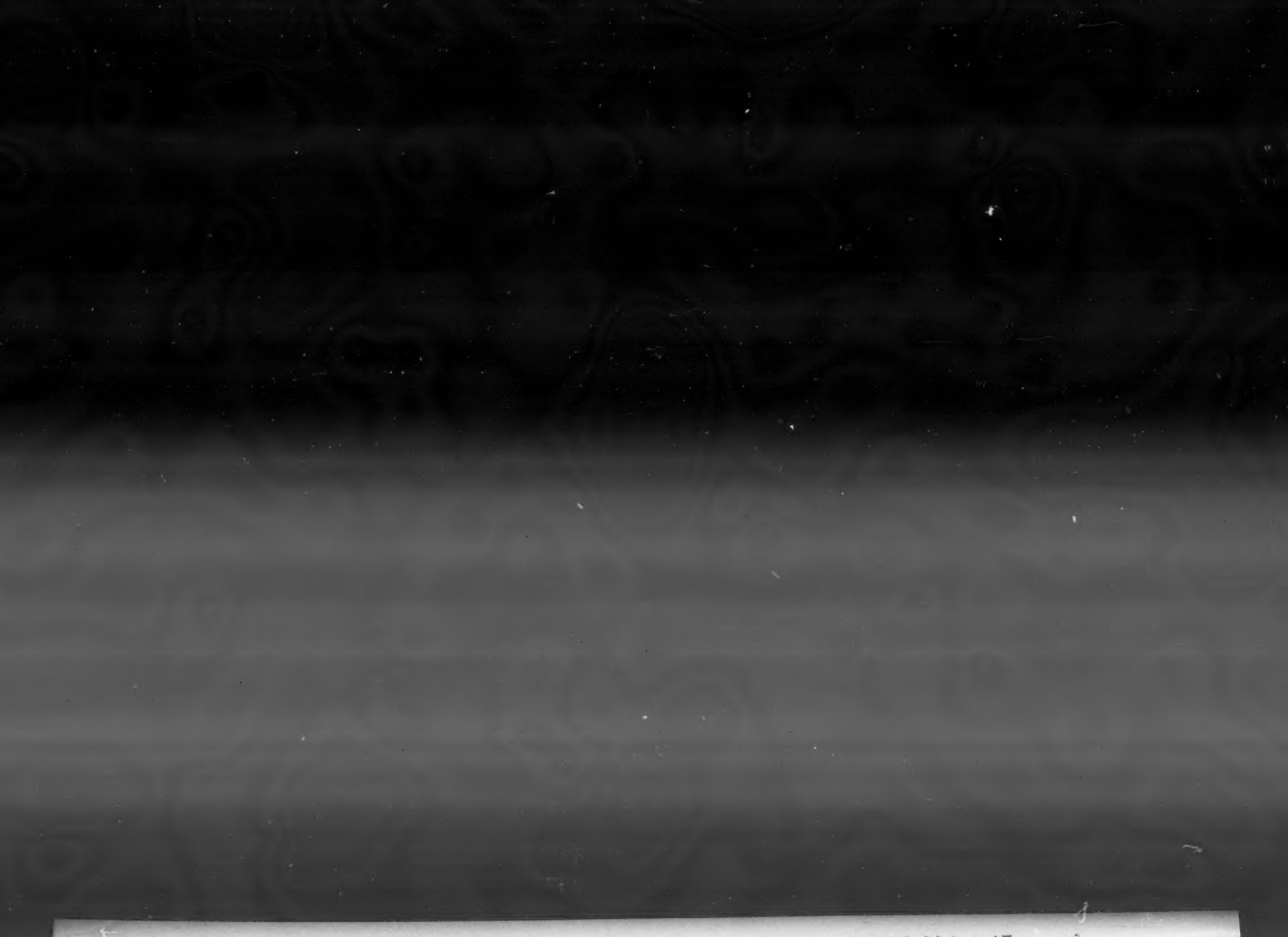


Snow crystals, natural and artificial

B. J. MASON

Although the delicate beauty of snow crystals, when seen under the microscope, has been known for many years, it is only comparatively recently that the mechanism of their formation has been studied. This article includes an account of a novel method of making permanent records of snow crystals by preparing plastic replicas, and gives an original theory of their growth. It appears that snow crystals react strongly to their environment, and present a faithful, though complicated, record of the changing conditions in the parent cloud.

The collection, examination, and classification of snow crystals has provided a fascinating field of study for many years, observations having revealed their great variety of shapes and forms. Until a very short time ago, however, little progress had been made in explaining this diversity, and in relating the external morphology of the crystals to the conditions of the environment. Early attempts to correlate the relative frequencies of the various crystal forms with the temperature at the place of observation gave inconclusive results, since only the conditions prevailing during growth of the crystals are relevant. The necessary information has recently become available, with the collection of snow crystals from all types of clouds having widely different conditions of temperature, supersaturation relative to ice, and vapour concentration.

As a complementary line of investigation, one may study the growth of ice crystals under carefully controlled conditions. It is, however, extremely difficult to simulate atmospheric conditions in the laboratory, and particularly to provide a realistic environment over a sufficiently long fall-path for the crystals to attain the size and complexity of the larger natural crystals. The simpler crystals, however, can readily be produced, though in miniature, by methods to be described later.

THE FORMATION OF SNOW CRYSTALS IN THE ATMOSPHERE

The ice elements formed in natural clouds are of three main types—individual ice crystals (or groups of crystals having a common nucleus), snowflakes, and hailstones. Every ice particle originates from a nucleus which may consist of a frozen cloud-droplet or a solid insoluble particle covered by a thin film of water which subsequently freezes. The properties and behaviour of these nuclei have been the object of considerable research [1]. After nucleation, the ice crystals continue to grow, in an atmosphere supersaturated relative to ice, by the diffusion of water vapour to their growing surfaces. They may exist as individual units of simple geometrical shape (e.g. hexagonal plates and prisms), or, under suitable conditions, may grow rapidly as dendritic forms into richly branching stellar crystals, several of which may collide and coalesce to form a snowflake.

There is a marked correlation between the external forms of the crystals and the characteristics of the parent cloud. The dominant crystal forms of the various cloud-types are shown in table 1, which is based largely on the observations of Weickmann [2]. The dominant crystal habit at temperatures below -25° C is the hexagonal prism (figures 13–16), which is indigenous to the high- and medium-level clouds. Those crystals which grow under conditions of high ice-supersaturation are generally distinguished by the presence of hollow cavities (figure 13), which are generally absent in the prisms collected from cirrostratus, where only slight supersaturations exist. At higher temperatures, the prisms give way to thin hexagonal plates, examples of which are shown in figures 7 and 18. In falling through the cloud, both plates and prisms may sweep up supercooled droplets which freeze on impact and endow the crystal surface with a rimed appearance (figures 9, 10, 15, 16). In a dense cloud containing a high concentration of droplets, the collisions are so frequent that the crystals quickly develop into irregular aggregates of soft hail or graupel (figure 17), which will attain a considerable size if the upcurrents of air support them in the cloud long enough; they are produced mainly in convective clouds. When a plate-crystal exceeds a certain diameter ($\sim 0{\cdot}2$ mm) it may, under suitable conditions, sprout at the corners to form a star-shaped crystal (figures 7–9). The arms of the star may propagate secondary branches to produce intricate

TABLE I

Classification of ice crystals according to shape, cloud type, and environmental conditions. (Based on Weickmann's observations [2].)

Crystal form	*Cloud type*	*Temperature* (° C)	*Humidity*[1] (*per cent. relative to ice*)	*Vapour pressure*[1] (*mb*)
Hollow prisms (mainly clusters)	Cirrocumulus Cirrus castellatus Cirrus uncinus	− 30 to − 50	135–165	0·50–0·06
Complete prisms	Cirrostratus	− 25 to − 50	75–100 (Water) 95–165 (Ice)	0·60–0·06
	Altostratus Altocumulus	− 25 to − 50	125–165	0·80–0·06
Thick plates	Altocumulus Altostratus	− 15 to − 25	115–125	1·9–0·80
Thin plates	Nimbostratus Stratus Stratocumulus	0 to − 15	100–115	6·0–1·9
Stars Needles (Dendritic forms)	Nimbostratus Stratocumulus	0 to − 15	100–115	6·0–1·9

[1] Calculated on the assumption that water saturation exists in all clouds except cirrostratus.

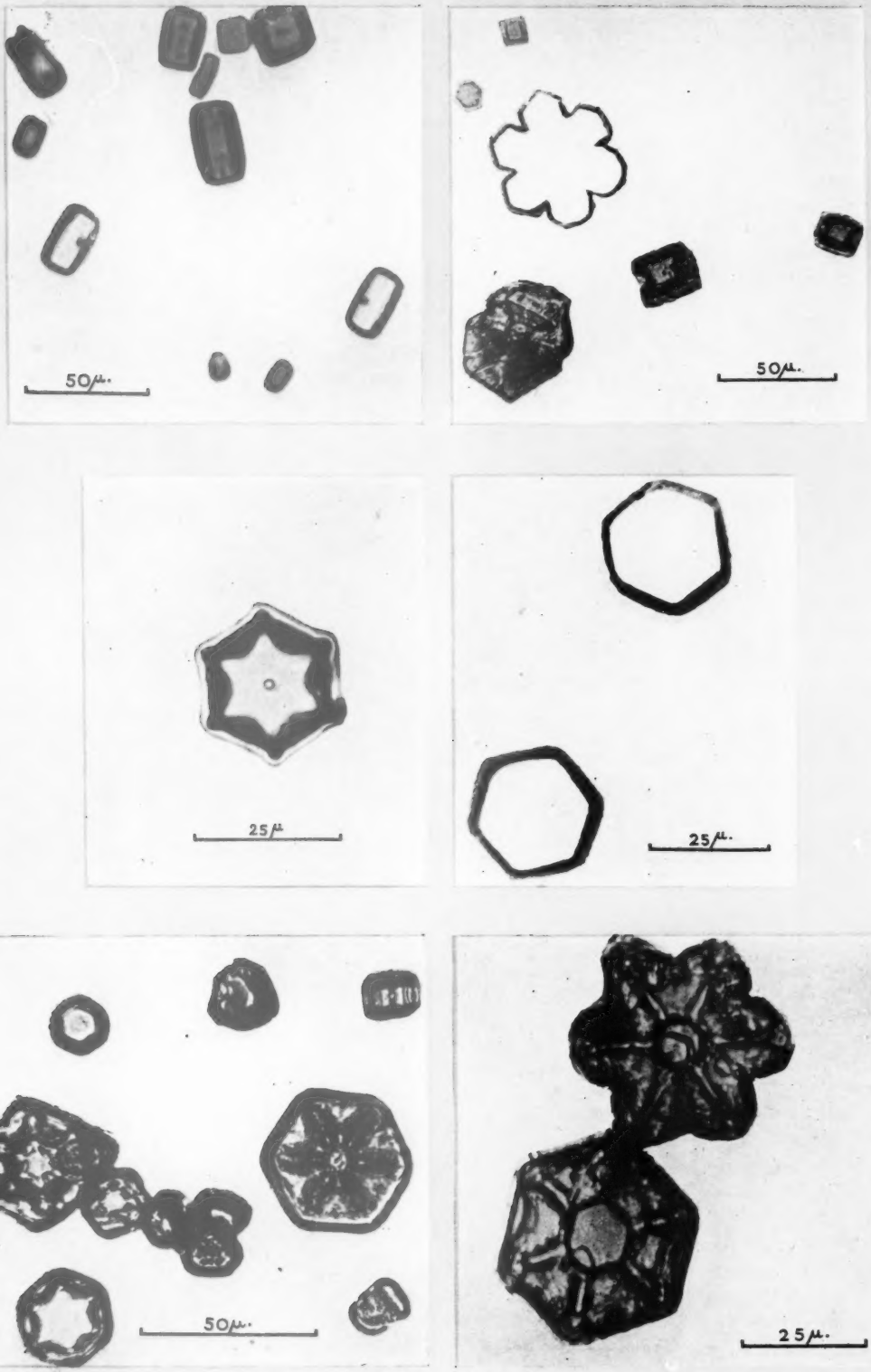
patterns of great beauty (figures 8–11). This secondary growth may continue until the spaces between the arms of the star become filled, except for small enclosed hollows, so forming a large plate-like structure, in the centre of which the original hexagonal crystal may often be identified (figure 9).

Snowflakes consist of a rather haphazard agglomeration of loosely interlocking crystals (figure 12). The individual components can often be identified and separated, which suggests that the flake is built up as a result of collision and subsequent coalescence of individual crystals having different terminal velocities; this process is greatly facilitated if the surfaces of the crystals are wet. Large snowflakes are thus to be expected when dendritic crystals are formed in 'warm' clouds of high vapour content (temperatures above about − 15° C) and fall into still warmer regions where coalescence occurs. In 'cold' clouds of low water content individual crystals will predominate.

Figures 7–12 and 14–18 show the form of some typical snow crystals which were caught at ground level during December 1950. They are, in fact, microphotographs of plastic replicas of the actual crystals, obtained by an ingenious technique devised by Schaefer [3]. A 1 per cent solution of Formvar (a polyvinyl acetal resin) dissolved in ethylene dichloride is kept at a temperature of about − 5° C. A clean microscope slide is immersed in the solution for about 30 seconds and then exposed horizontally to the falling crystals. A captured crystal becomes submerged in the solution, and if the slide is kept at sub-freezing temperature for a few minutes the solvent evaporates, leaving the crystal encased in a thin but tough plastic shell. Once the solvent has evaporated the slide may be exposed to room temperature, when the crystal will melt, the water diffusing out through the plastic membrane as it evaporates, to leave a replica which retains in microscopic detail all the surface configurations of the original crystal (see especially figures 7–11). The crystals are also easily caught on a black cloth, when replicas of selected specimens can be made by touching them gently with a plastic-coated slide. The replicas may be stored indefinitely and photographed at leisure. Figures 7–12 and 14–18 were obtained by photographing the replicas through a low-power microscope, using reflected light.

PRODUCTION OF ICE CRYSTALS IN THE LABORATORY

Small crystals of less than 50 μ diameter, yet possessing many of the characteristics of natural



FIGURES 1–6 – *Photomicrographs of a variety of ice-crystal forms produced by seeding a supercooled water cloud with solid carbon dioxide.*

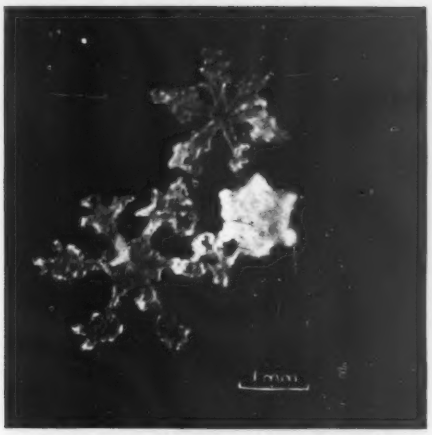


FIGURE 7 – *Crystals showing early stages of dendritic growth, and a single plate covered with rime.*

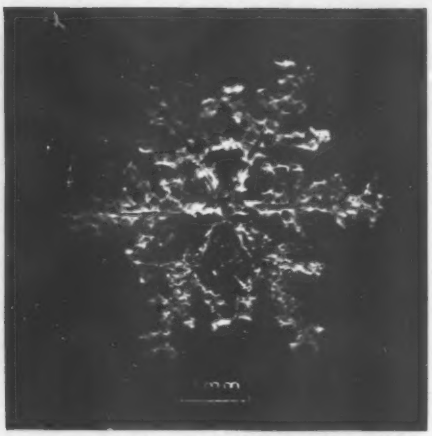


FIGURE 8 – *A crystal showing advanced dendritic growth.*

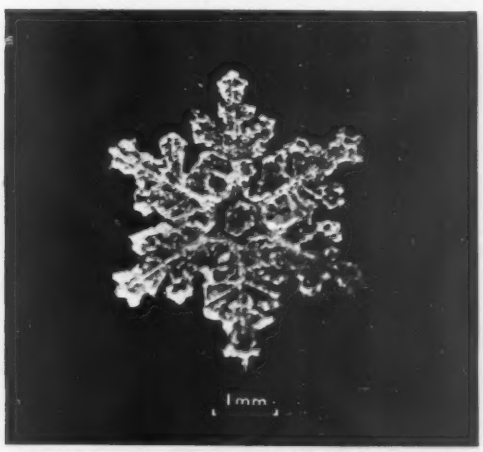


FIGURE 9 – *A stellar crystal showing the hexagonal plate at its centre.*

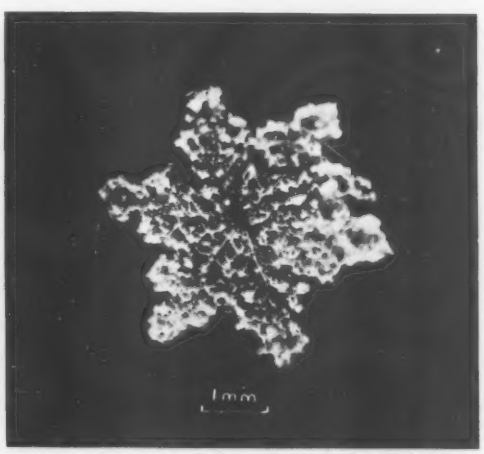


FIGURE 10 – *A stellar crystal covered with frozen droplets.*

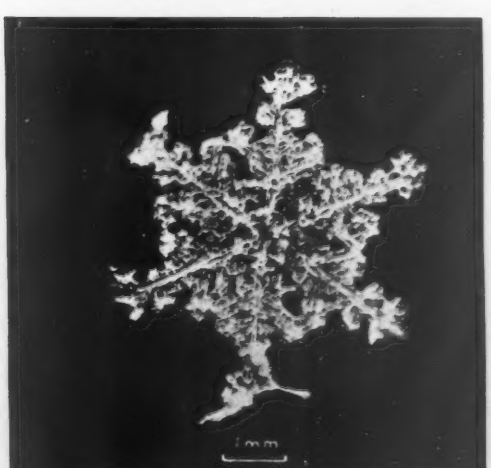


FIGURE 11 – *A stellar crystal showing the space between the arms filled in, except for small enclosed hollows.*

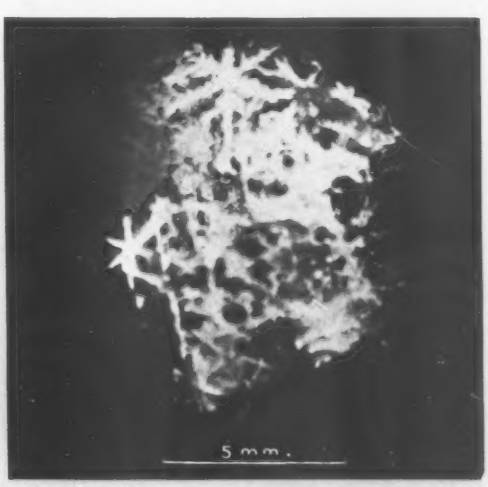


FIGURE 12 – *A snowflake composed mainly of interlocking stellar crystals.*

FIGURE 13 – *Hollow prismatic crystals (after Weickmann* [2]).

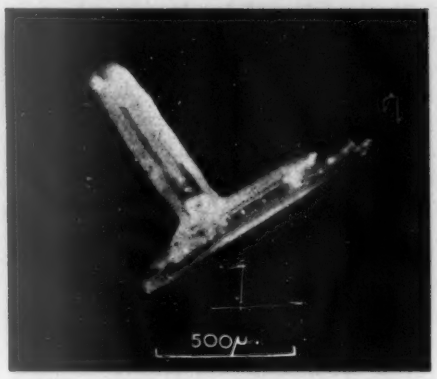
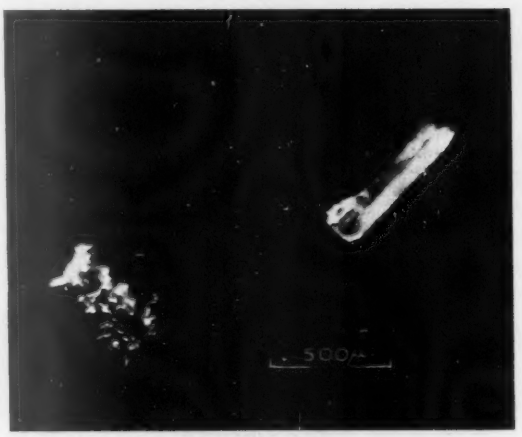


FIGURE 14 – *Large prismatic columnar crystals.*



FIGURES 15 *and* 16 – *Prismatic crystals covered with frozen droplets (rime).*

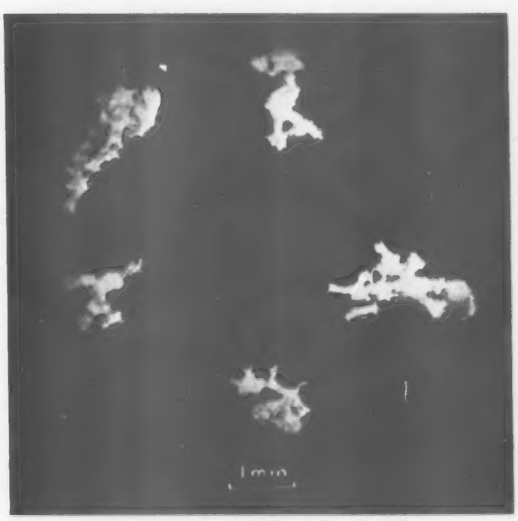


FIGURE 17 – *Pellets of soft hail.*

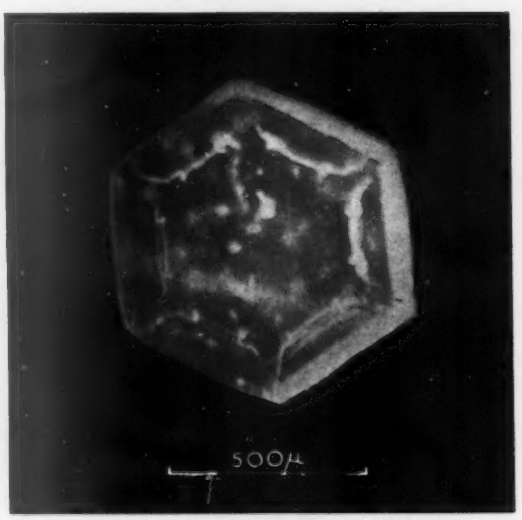


FIGURE 18 – *A single hexagonal plate.*

crystals, may be produced in vast numbers with extremely simple apparatus. The method is to produce a cloud of minute supercooled water droplets in a cold chamber and to transform this into a cloud of small ice crystals by introducing a seeding agent.

One simple apparatus used by the author consists of a thermally insulated double-walled copper chamber, of some 20 litres internal capacity; the lower half of the annular space is filled with a cooling mixture of petrol and solid carbon dioxide. The bottom of the chamber may thus be cooled to about — 45° C, though — 20° C is a convenient temperature for most experiments. The chamber may be used with the top open, the strong temperature inversion making the air inside very stable. A supercooled cloud may be produced by breathing into the chamber or by evaporating water from a small container. The cloud, which is composed of droplets of some 10 μ diameter, at a concentration of a few hundreds per cubic centimetre, is illuminated by a powerful parallel light beam, the walls of the chamber being lined with black velvet to provide dark background illumination. As a more convenient, but much more expensive, form of this apparatus one may use a thermostatically controlled low-temperature refrigerator.

At — 20° C the supercooled water cloud persists for several minutes, and only an occasional ice crystal is seen to glitter in the light beam. If, however, any part of the chamber is cooled below about — 40° C, large numbers of ice crystals appear, the water fog being transformed completely into ice crystals within a few seconds.

Schaefer [4] claims that the transition is very sharp, a pellet of mercury (melting point — 38·9° C) leaving ice crystals in its wake as long as it remains solid, but not after the instant of melting. He interprets this temperature as the critical temperature at which ice crystals arise spontaneously from the vapour. It seems difficult, however, to associate such a statistical event with a sharp transition temperature. In fact, the present author [8] finds that only a very few ice crystals appear at — 39° C, and that the number increases rapidly with falling temperature, very large numbers being formed at — 41° C. It seems that the rapid chilling produces a momentary supersaturation high enough to cause spontaneous condensation, and that the droplets quickly evaporate unless they freeze spontaneously into crystals which, even at the original temperature, are in a supersaturated atmosphere and therefore survive and continue to grow to visible size. This view is supported by the fact that small water droplets (~.10 μ) suspended in air freed from foreign nuclei can be cooled down to — 40·5 ± 1·5° C before freezing [5].

The transition from a supercooled water cloud to an ice cloud may be demonstrated in a very striking manner by scratching a single tiny speck from a piece of solid carbon dioxide (temperature about — 65° C) into the chamber. The track of the pellet first shows as a thin white streak, which broadens rapidly and after a few seconds takes on the beautiful appearance of a condensation trail; this may be compared with the trail left by an aircraft. The appearance of the lower edge of the trail suggests that the pellet of carbon dioxide, by cooling the top of a thin layer of air, has caused it to become unstable and to break up into small pockets of cold air which carry some of the minute crystals downwards.

At this stage, countless numbers of tiny ice crystals can be seen glittering in the vicinity of the trail, and within a few seconds they become dispersed throughout the cloud by local convection currents and turbulence. As the equilibrium vapour pressure over a water surface exceeds that over an ice surface at temperatures below 0° C, the mixed cloud of water droplets and crystals is colloidally unstable; the droplets evaporate and the vapour sublimes on to the crystals, which grow quite rapidly and fall to the bottom of the chamber. The above experiment demonstrates very clearly those physical processes which are fundamental to the release of precipitation from the majority of natural clouds, and also exactly what happens when pellets of solid carbon dioxide are dropped into clouds with the object of inducing precipitation artificially. A small speck of solid carbon dioxide may produce some 10^7 crystals when introduced into a supercooled cloud at — 20° C. Photomicrographs of replicas of some typical crystals, which in this case were viewed by transmitted light, are shown in figures 1–6. They consist for the most part of small hexagonal plates and short hexagonal prisms, and are in many respects just miniatures of similar atmospheric crystals. Although the dimensions of many crystals are only a few microns, the replicas reveal detailed surface markings and internal cavities.

THEORY OF SNOW CRYSTAL GROWTH

An attempt has recently been made by the author [6, 7] to explain the development of the various crystal forms in terms of their molecular

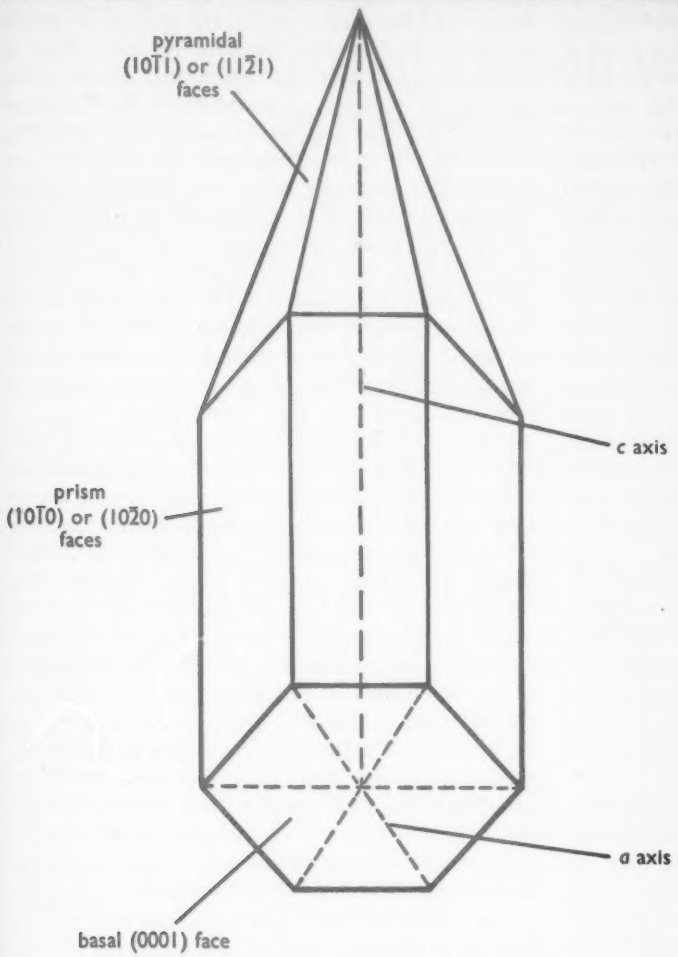


FIGURE 19 – *The crystallographic faces of ice.*

and surface structures, their fall-motion, and the meteorological conditions in the parent cloud.

The rate of growth of a snow crystal is determined by the rate of arrival of vapour by diffusion, and by the rate at which the molecules can be assimilated into the surface structure, which in turn is controlled by the rate at which the latent heat of crystallization can be dispersed, mainly by conduction through the air. The computation of the growth-rate of, say, a falling plate-crystal is a difficult problem. If, as a first approximation, its surface is regarded as an equipotential, and the fall-motion of the crystal is neglected, the rate of increase of mass m is given by

$$\left(\frac{RT}{DMP}+\frac{L^2\mathcal{J}M}{KRT^2}\right)\frac{dm}{dt}=8r\sigma \quad \ldots\ldots \quad (1)$$

where M is the molecular weight of ice, D the coefficient of diffusion of water vapour in air, K the thermal conductivity of air, P the vapour pressure, σ the supersaturation, T the temperature, R the gas constant, L the latent heat of crystallization, $\mathcal{J}$ the mechanical equivalent of heat, and r the crystal radius. The rate of increase of mass of a plate-crystal is thus less than that of a sphere of equivalent radius by a factor of $2/\pi$. The lines of diffusive flux will be concentrated at the edge of the disk, so that its thickness x will increase only very slowly; assuming it to remain constant, the rate of change of radius is given by

$$\left(\rho\frac{RT}{DMP}+\frac{L^2\mathcal{J}M}{KRT^2}\rho\right)\frac{dr}{dt}=4\sigma/\pi x \ldots (2)$$

where ρ is the crystal density. At $T = 260°$ K and water-saturation, and with $x = 10\,\mu$, $dr/dt \sim 7 \times 10^{-5}$ cm sec^{-1}, so that the crystal will grow to a radius of $100\,\mu$ in about 150 seconds. The growth-rate will be slightly greater than predicted by equation 2 if the crystal is falling.

From the molecular structure of ice, as revealed by X-ray and neutron diffraction, it appears that its mean crystalline structure belongs either to the dihexagonal-bipyramidal (D_{6h}^4) or to the ditrigonal-bipyramidal (D_{3h}^4) space group. The dominant growth-forms to be expected are therefore hexagonal prisms, hexagonal bipyramids, and hexagonal prisms with pyramidal ends (see figure 19). The external morphology of a crystal is determined, however, by the relative rates of growth of the different faces; the pyramidal faces, being of lower atomic density (i.e. of high index), will in general grow faster than the basal and prism faces, and so tend to grow out. The dominant crystal habit of an ice crystal should therefore be a hexagonal prism bounded by the slow-growing (0001) and (10$\bar{1}$0) or (11$\bar{2}$0) faces, and this is certainly the most common basic shape among atmospheric crystals. The pyramidal faces may persist for some time when the crystal is growing slowly; in fact the formation of certain rare haloes in cirrostratus can be explained by the refraction of light in pyramidal crystals.

The prismatic crystals which predominate

below — 25° C develop as a result of preferential growth along the principal (c) axis, i.e. normal to the basal (0001) face. It is suggested that the most important factor in determining the relative rates of growth of different faces is the relative rates at which molecules diffuse along the surfaces towards their respective growth-fronts; this in turn will be controlled largely by the activation energy which is necessary for a molecule to jump over the potential peaks of the surface field. Exact calculations of the fields of force at the various crystal faces of ice have not yet been made, but there is indirect evidence that the coefficient of surface diffusion will be greater on the basal face. Hence, given an equal current of molecules to both faces, the basal face will be propagated faster than a prism face, leading to the development of prismatic columns.

The plate-crystals, on the other hand, are produced as a result of the growth normal to the basal face being overshadowed by a much more rapid development in the direction of the secondary (a) axis. Weickmann [2] has suggested that at higher temperatures the molecules striking the basal face do not form a new layer but diffuse across the face and are built into the crystal structure only at the edges. The fact that molecules migrate from one crystal face to another is now well established, and it can be shown that the ratio between the rates of propagation of the edges of the crystal by surface diffusion from the basal faces and by direct deposition from the vapour is given by $2\lambda/x$, where λ is the average distance a molecule travels on the surface before evaporating, and x is the thickness of the plate. Surface diffusion will be the dominant process if $x < 50$ μ. The thin ice plates formed at temperatures above — 20° C have thicknesses of about 10 μ, so that migration of molecules from the basal faces to the edges may be a significant factor in their development. This effect will be reduced at low temperatures, as indicated by the formation of 'glassy' ice at temperatures below about — 70° C. Once the plate-like development has begun it will be further assisted by the concentration of the lines of diffusive flux towards its edges.

The dendritic stellar crystals often arise from small hexagonal plates, the corners of which shoot out to form the arms of the star. Such a development marks the beginning of dendritic growth, as opposed to the ordered development of crystal faces leading to polyhedral growth, which occurs only if the diffusion field is not disturbed appreciably from its equilibrium state. The falling crystal will, however, disturb the field, which will strive to return to its equilibrium pattern with a speed determined by the coefficient of diffusion. If, however, the crystal falls at an appreciable speed, non-uniform gradients will be set up, and the rate of arrival of vapour at the crystal surface will be reduced. If the material is extracted from the field faster than it can be replaced by diffusion, the concentration in the immediate neighbourhood of the crystal will fall below the equilibrium value and only the corners will grow, since they protrude into regions of higher concentration. Polyhedral growth thus breaks down and dendritic growth begins. The diffusion field will now reorganize itself and become highly convergent towards the growing tips, which also will be preferred sites for the dissipation of the latent heat of crystallization. The criterion for the onset of dendritic growth must express the much greater tendency for the diffusion field to be disturbed by the falling crystal than for it to return to its equilibrium condition. The author [7] shows this criterion to be $vr/D \gg 1$, where v is the velocity of the crystal relative to the air, r the crystal radius, and D the coefficient of diffusion. The terminal velocity of small hexagonal plates in still air is about 30 cm sec^{-1}, and $D \sim 0{\cdot}3$ cm^2 sec^{-1}; thus dendritic growth will set in only when r considerably exceeds 0·1 mm, which is in good agreement with observation. In order to grow into large dendritic structures the crystals must spend a considerable time in a cloud of high vapour-concentration; in view of their relatively high speeds of fall, the cloud must also be of considerable depth. Snow crystals appear to react strongly to their environment, and to present a faithful, if complicated, record of the changing conditions in the parent cloud.

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The analysis of inorganic compounds by paper chromatography

F. H. POLLARD and J. F. W. McOMIE

Although inorganic analyses on strips of absorbent paper were described a century ago, it is only within the last few years that the possibilities of the method have been closely examined. This overdue examination has proved very rewarding, and methods of separating a very wide range of mixtures of cations have been developed. The results are comparable with those achieved by orthodox analysis, but the methods are very much more economical of both time and material. It appears that similar techniques can be developed for anions.

Recent researches [1a] into the early history of chromatography indicate that the first recorded experiments on capillary analysis should be attributed to F. F. Runge, who, in 1850, analysed mixtures of dyes on blotting paper, and earlier had suggested spot tests for bleaching solutions, using dyed cotton fabric or paper impregnated with starch and potassium iodide. His interest also extended to the possibilities of using the capillary ascent of solutions in blocks of wood for the separation of solutes. At a later date this was more fully investigated by Goppelsroeder, a pupil of Schoenbein [1b]. The latter, who has usually been regarded as the pioneer of capillary analysis of inorganic compounds, showed that if a strip of paper is dipped into water containing inorganic salts, the water rises in the paper and carries the salts with it. The liquid front usually advances ahead of the inorganic cations, which move independently according to their relative rates of diffusibility. The types of separation achieved are illustrated in figure 1. Two simple techniques can be used. The first consists in dipping an inch-wide strip of filter paper, with a spot of the mixture of cations placed about one inch from the lower end, into a small beaker of water; the water is allowed to rise in the strip by capillary action. Some results obtained by this method are illustrated in figure 1 (*a*), (*b*), and (*c*). In the second technique one uses a disk of filter paper placed between two glass plates, about six inches square, gripped together by clips; the upper plate has a hole in the centre [2]. One drop of the mixture of cations is placed on the paper through the hole, and is followed by drops of water or other solvents, such as methylated spirit. This procedure has the advantage of being very quick, giving sufficient movement of the liquid front in about fifteen minutes, compared with several hours for other methods. Such disk-separations are illustrated in figure 1 (*d*) and (*e*). In general, the difference in the rates of diffusion of different cations is not sufficient to produce a clean separation, and the bands containing the cations are often very close together or overlapping. Nevertheless, with certain mixtures, for example of lead, silver, and nickel or cobalt, it is possible to get sufficient separation for purposes of identification (see figure 1 (*d*)). With some cations, hydrolysis may occur, and the solvent must be acidified to prevent it; the *p*H of the mobile phase may, therefore, be quite a critical factor. Hydrolysis may be used to separate the cation from the anion; with lead acetate, for example, the acetate anion will move away from the lead hydroxide, which is retained at the starting point. On the whole, the process is not so successful with inorganic salts as with materials like organic dyestuffs, which, as Goppelsroeder [3] showed, can be separated into distinct and completely detached zones.

TABLE 1

Reagents used to identify cations in the chromatograms illustrated in figures 1–3

Reagent	*Cations*
Rubeanic acid	Ni—greyish blue; Cu—olive green; Co—brown
Potassium chromate	Pb—yellow; Ag—brick red
Potassium thiocyanate	Bi—yellow
Potassium ferrocyanide	U—purplish brown; Fe—blue
Rhodizonic acid	Ba—bright red; Pb—violet
Phosphomolybdic acid	Sb—blue
Sodium hypophosphite	As—brown
Zinc uranyl acetate	Under ultra-violet light. Na—bluish-green fluorescence
Kojic acid and 8-hydroxyquinoline	Under ultra-violet light. Al—green fluorescence; Sn—yellow fluorescence.

NOTE. For further details see reference [12].

Schoenbein's work aroused the interest of

E. Fischer [4], who carried out a quantitative investigation of the separation of sodium and barium, and of certain double salts, on a column consisting of six individual rolls of filter paper packed closely together. He observed that some separation occurred, as is shown by the results quoted for a solution containing equal concentrations of barium and sodium chlorides:

Roll No. ..	1	3	5
$BaCl_2/NaCl$ ..	1 : 1·022	1 : 1·230	1 : 1·364

He utilized this method in order to separate the cations in a double salt such as ferrous ammonium sulphate, thus demonstrating the absence of a complex ion.

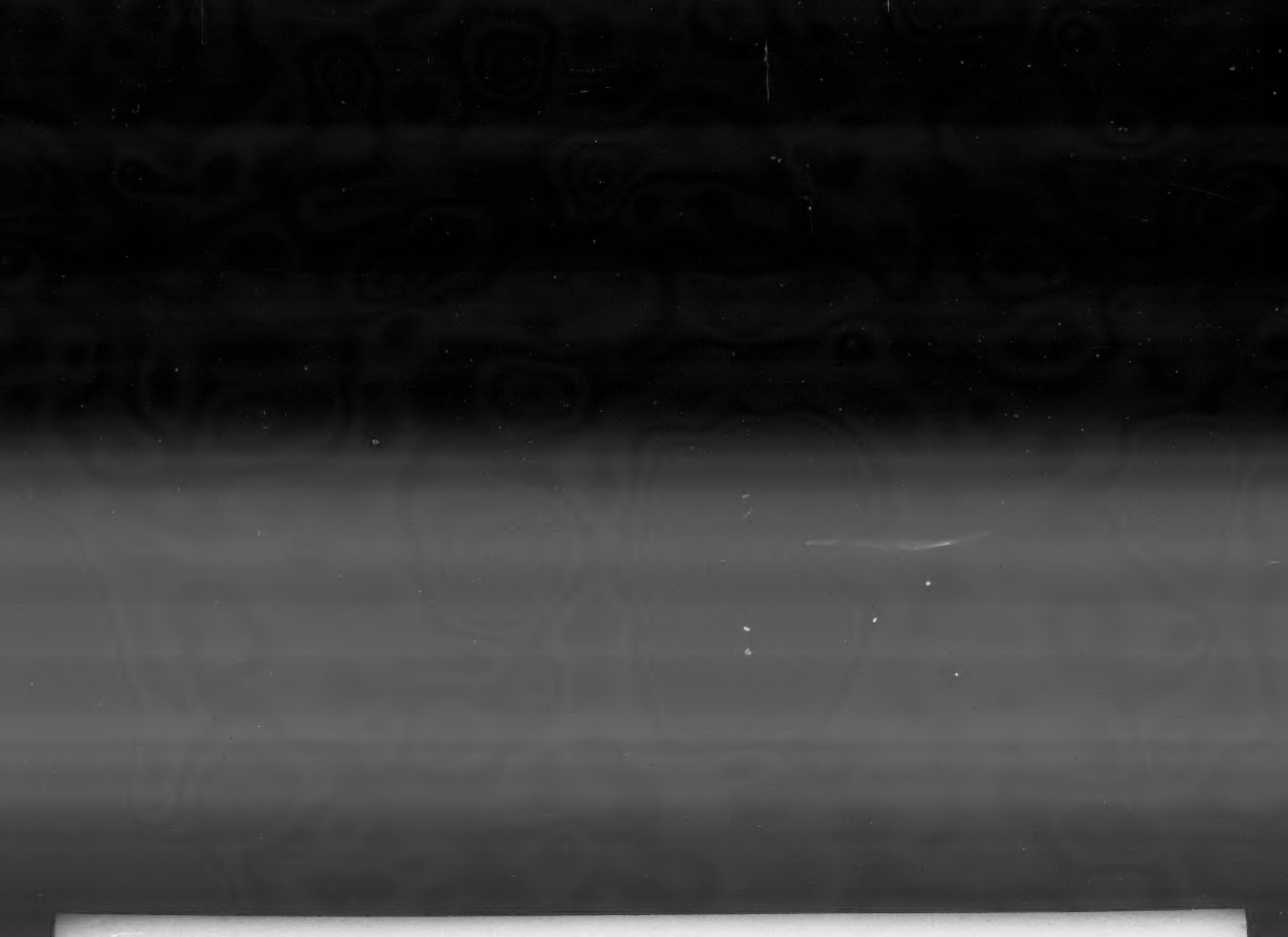
More recently, Flood [5] has carried out extensive researches on separations with paper impregnated with alumina, in which he has obtained zones of cations similar to those on alumina columns described by Schwab and Jockers [6]. The method consists in dipping an alumina-impregnated strip of paper into a solution of the cations and allowing the water to rise in it by capillary action. As the liquid rises, the more strongly adsorbed cations displace the weaker ones, which are pushed ahead, forming distinct zones. The process is essentially displacement chromatography, the length of the zone being proportional to the initial cation concentration. Flood has used this method to estimate quantitatively the strengths of solutions.

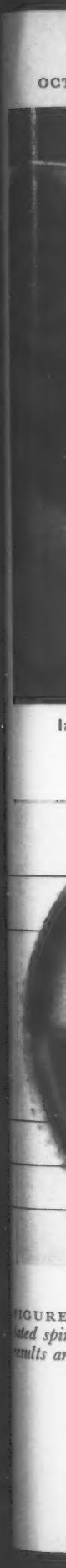
Except for the occasional use of capillarity for certain microchemical tests, no marked advances were made until recently, when a number of independent workers, inspired by the outstanding successes in organic chemistry of the Martin and Synge [7] partition techniques, reinvestigated these methods. The basis of the separation of organic substances was that of differential partition between an organic solvent and water, the latter being carried on an inert support such as cellulose—often in the form of filter paper—as a diffusion medium. While the procedures employed for inorganic compounds resemble those for organic compounds, there is no crucial experimental evidence to suggest that the separations are entirely due to differential partition. Some of the procedures described, however, such as the separation of uranyl nitrate using ether as solvent, do apparently depend essentially on selective extraction. To what extent adsorption or exchange is involved in the separations is still not at all clear, though it may be that dipolar interaction occurs between hydrated ions and the imbibed water on the cellulose of the same type as that suggested by Sacconi [8] for alumina. This aspect of the function of the cellulose support has been discussed by Hanes and Isherwood [9]. Some workers recommend special conditioning treatment for the cellulose, but for the solvent mixtures employed by us we have found that no advantages accrue from such treatment. All the examples illustrated here were obtained with untreated Whatman No. 1 filter paper. The important point is that, whatever the mechanism concerned, the behaviour of the inorganic compound in a particular chromatogram is definitely reproducible, except where, in the presence of certain other compounds, displacement occurs. Such displacements as we have noticed are not very serious, and often bring about an improved separation.

The movement of the compounds is conveniently expressed in terms of their R_f value, which measures their rate of movement relative to the liquid front. The R_f value is a constant for a particular cation with a particular solvent-mixture as the mobile phase, provided that all essential conditions, notably grade and condition of paper, temperature, distance moved by the solvent front, and pH of the mobile phase are maintained constant.

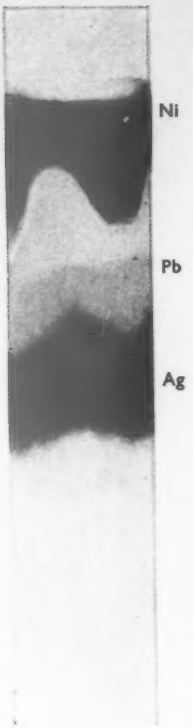
For qualitative work the apparatus and general procedure are based on those of Martin and Synge. A trough of glass or plastic material is supported in a glass tank which can be made airtight by a glass plate. The solvent is put in the trough, and a sheet of filter paper, with spots of the solution to be analysed placed on a line drawn about two inches from the top of the paper, is hung with the upper end dipping into the solvent. The solvent siphons over and down the strip, and, when the solvent front is about an inch from the bottom of the paper, the sheet is removed, dried, and sprayed with the reagents necessary for the identification of the various ions. Provided that adequate precautions are taken to keep the paper reasonably taut, upward movement of the solvent, like that used originally by Schoenbein, and the disk method can both yield good chromatograms.

The choice of solvent mixture for the mobile phase determines the extent, and often the order, of separation of the inorganic cations. Many different types of organic liquids have been tried, but the choice of new solvents for investigation will depend upon the particular cations in the initial mixtures, and upon the kind of process, namely extraction or partition, which is considered to be responsible for the separation.





Ia



Ib

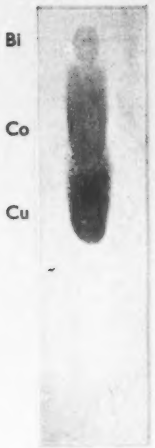
Ic

Id

Ie

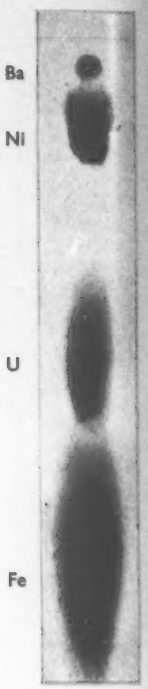
FIGURE 1 – *Fairly good separations of some metals can be obtained on filter paper by capillary action, using water or solvents like methylated spirit as the developing liquid. The examples illustrated show that the bands are usually close together and often overlap. Similar results are obtained with either the strip (figure* 1a, b, *and* c) *or the disk (figure* 1d *and* e) *techniques, but the latter is much quicker.*

2a



2b

2c



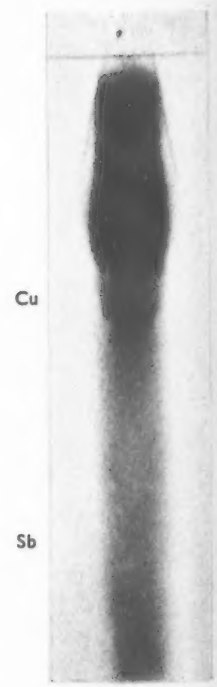
2d

FIGURE 2 – *Separations by partition chromatography show much clearer bands, usually some distance apart. The use of a complexing agent in the mobile phase (e.g. benzoylacetone in aqueous butanol) facilitates the separations, since the various metal complexes are likely to have markedly different partition coefficients for distribution between the water and the organic solvent. The order of separation is different from that with water alone.*

3a (i)

3a (ii)

3a (iii)



3a (iv)

FIGURE 3 – *Unknown mixtures of cations can be analysed by using a suitable series of identification tests on a number of similarly prepared chromatograms (see table I).* (a i–iv) *Mixture of Ag, Pb, Ni, Cu, Sb, and Ba;* (b i and ii) *mixture of Al, Cu, As, and Sn;* (c i–iii) *mixture of Al, Na, U, Fe, and Sn. The mobile phase used here was a mixture of benzoylacetone and aqueous butanol.*

3b (i)

3b (ii)

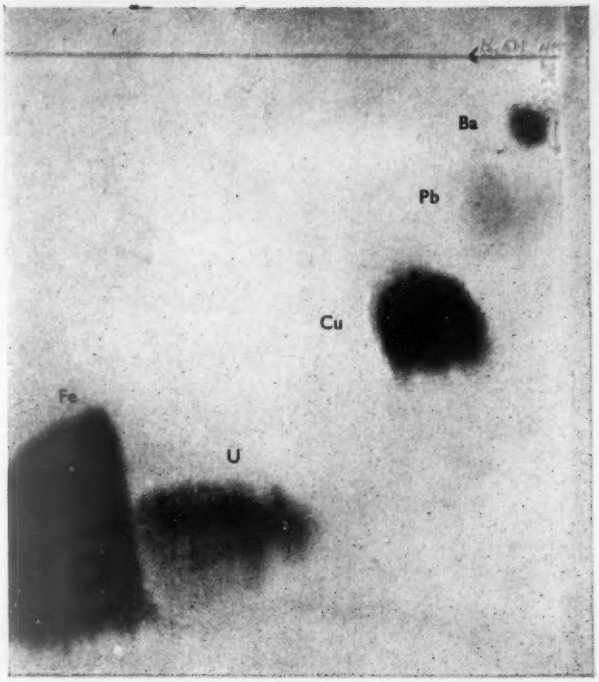


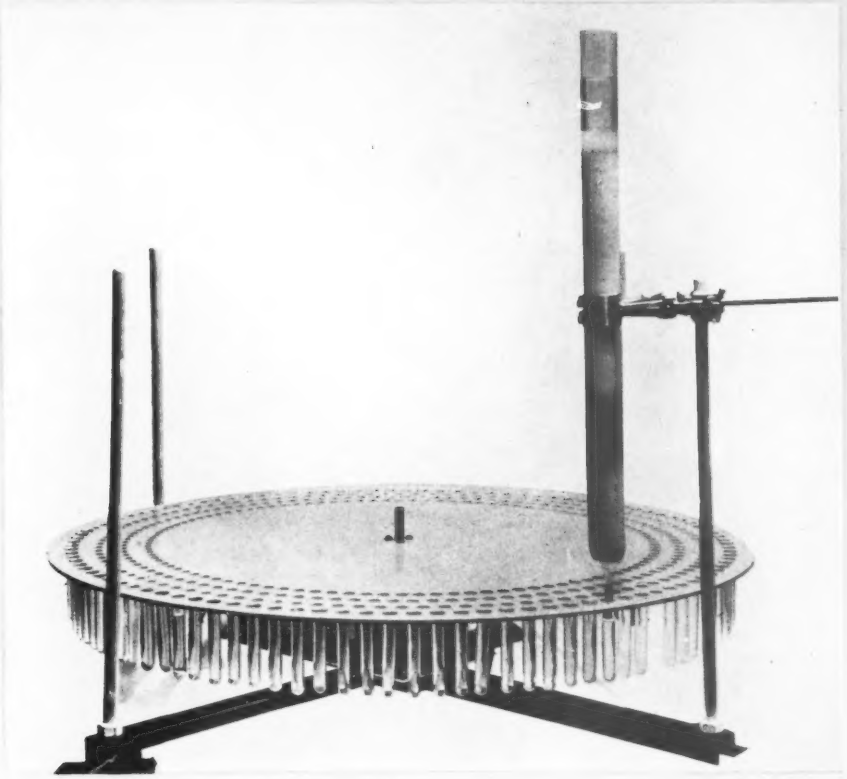
FIGURE 4 – *Two-way separations can often produce improved chromatograms. The example shows a chromatogram prepared in one direction with aqueous butanol containing benzoylacetone, and in the other with aqueous butanol containing trichloracetic acid.*

3c (i)

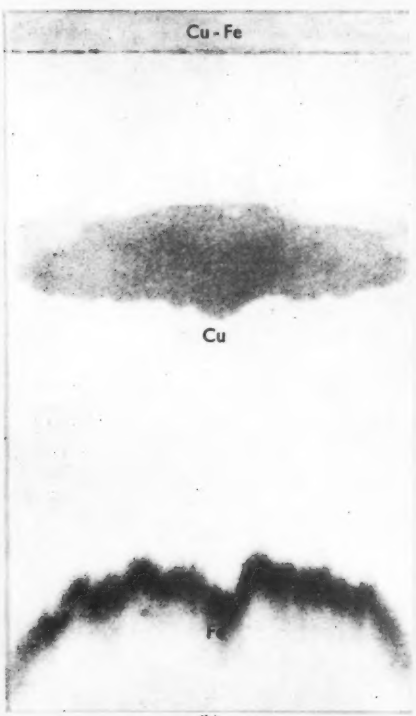
3c (ii)

3c (iii)

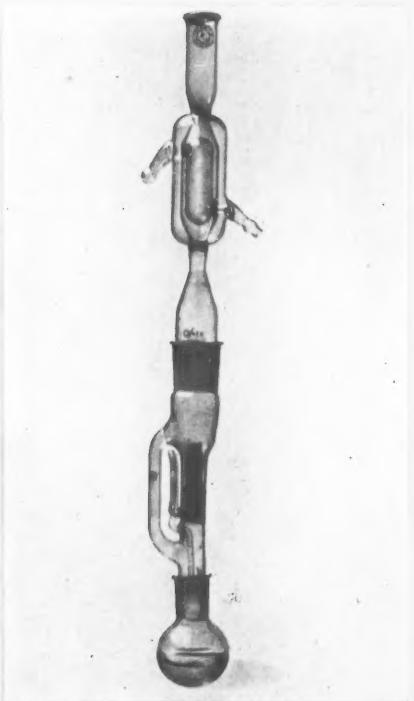
FIGURE 5 – *Some anion separations.*



(a)



(b)



(c)

FIGURE 6 – *Paper chromatography can be used for quantitative inorganic analysis.* (a) *Automatic fraction collector used for collecting fractions separated on a column of cellulose.* (b) *Paper chromatogram for quantitative analysis. Using a micro-pipette, a known volume of the copper-iron solution is placed along a pencil line in a series of spots. The paper is run with benzoylacetone in butanol as the mobile phase, dried, and the coloured bands due to the coloured benzoylacetonates are cut out and then extracted individually in the Soxhlet apparatus* (c) *with ethyl alcohol. The respective extracts are analysed colorimetrically.*

Clearly, the solubility of the inorganic compound in the organic solvent will largely determine how far the particular compound will move from the starting line. Very soluble compounds will move with, or closely behind, the solvent front; less soluble compounds will move to intermediate positions; insoluble compounds will not move at all. To effect a good separation, therefore, there must be an appreciable difference in the respective solubilities, especially if selective extraction plays the major role; if partition effects are important, a slighter difference in the solubilities may produce efficient separation as a result of the repeated partition between the mobile phase and the stationary water held by the paper. While a number of inorganic salts are soluble in organic solvents, it is probable that some salts dissolve as a result of the formation of a soluble complex with the solvent itself. Thus copper chloride will dissolve in butanol saturated with 3N.HCl and moves with an R_f of 0·19, but with collidine it forms a complex and moves with an R_f of 0·76. The deliberate addition of a complex-forming reagent to a solvent mixture can be most effective in separating metals, different complex-forming agents changing the extent of the separation. Whenever complex-formation is employed, the stability of the complex must be assured by the adjustment of the mobile phase to the correct *p*H. A complicating factor, the effect of which cannot be precisely assessed, is that, when a mobile phase containing acid moves down the paper, two fronts can be detected, the upper one being due to the partial retention of the acid by the paper. This may well affect the stability of some of the complexes, with a resultant change in their R_f values.

There have been two distinct lines of approach to the use of paper chromatography for analysis. One is devoted to the separation of the groups of cations associated with the orthodox qualitative analysis, and the other to the development of a scheme which does not depend upon any previous separations. In table II is given a scheme for the former, based on the work of Linstead [10], Lederer [11], and others; it illustrates the various types of solvent employed.

The second approach to the problem of separations dependent entirely on paper chromatography has been made by the Bristol (England) school [12], and is based on the behaviour of a large number of cations with solvents containing a complexing reagent, or with those capable themselves of forming complexes. Three organic solvents—butanol, collidine, and dioxan—have been carefully studied, and it has been found that the cations or their derivatives can be divided into groups, depending on the mobile phase used.

TABLE II

	Solvent	*Mixture separated*
Group 1	Aqueous ammonia.	Pb, Ag, Hg
Group 2*a*	Butanol saturated with 3N.HCl, or ethyl *iso*propylketone with 10 per cent. HCl.	Hg, Bi, Cd, Cu, Pb
Group 2*b*	Butanol saturated with 3N.HCl, or ethyl acetate with 2 per cent. HCl, or acetylacetone saturated with water + 0·5 per cent. by volume of conc. HCl and 25 per cent. by volume of acetone.	Sn, Sb, As
Group 3	*Either* (*a*) Glacial acetic acid + 25 per cent. by volume of methyl alcohol; (*b*) Acetone containing 5 per cent. by volume of water and 8 per cent. by volume of conc. HCl (specific gravity 1·18). *Or* (*a*) 80 per cent. methyl *n*-propyl ketone, 10 per cent. acetone, and 10 per cent. conc. HCl; (*b*) Butanol-acetic acid.	(*a*) Fe, Al, Cr (*b*) Ni, Mn, Co, Zn (*a*) Fe, Co, Mn, Ni (*b*) Cr, Zn, Al
Group 4	Pyridine containing 20 per cent. by volume of water and 1 per cent. KSCN.	Ca, Sr, Ba
Group 5	Methyl alcohol.	Li, Na, K

Group I. Cations moving with butanol-water-benzoylacetone mixture.

Ag^{+}, Hg^{+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sn^{2+}, Sn^{4+}, Fe^{3+}.

Group II. Cations moving with collidine-water mixture.

Ag^{+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}, K^{+}, Na^{+}.

Group III. Cations moving with dioxan-antipyrine mixture.

Ag^{+}, Hg^{+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sn^{2+}, Sn^{4+}.

Although some inorganic compounds move in all solvents, the extent of the movement may be quite different in each. This has marked advantages for analytical purposes.

Two different schemes of procedure have been evolved. The first consists in preparing chromatograms with each of the three solvent mixtures, and identifying the cations by their approximate R_f values and characteristic reactions. The second is based on a sequence of characteristic reactions applied to a number of chromatograms prepared with the butanol-water-benzoylacetone mixture (see table III). Illustrations of the latter are given in figure 3.

As an almost universal reagent for the detection of cations on paper, a mixture of 8-hydroxyquinoline and kojic acid has proved invaluable; it yields complexes which fluoresce or give dark spots in ultra-violet light. The behaviour of a cation with this reagent, coupled with a measurement of its R_f value, is often sufficient for its identification. In addition, many of the standard identification tests (see table I) can be adapted for the detection of ions on filter paper, often with an increase in sensitivity. Some examples are illustrated, but fuller details are available in the published papers. The smallest amount of material which can be chromatographically separated is partly determined by the sensitivity of the identification test; as a rough guide this minimum quantity may be said to be about four times the sensitivity of the test. For example, with cadmium the limit would be about $0{\cdot}2 \times 10^{-6}$ g if detected with the fluorescent reagent, but about 1×10^{-6} g if hydrogen sulphide were used.

The different behaviour of cations with different solvent mixtures as the mobile phase can be used to advantage for two-way processes which will yield improved separations for cations otherwise lying close together. Not only can two different organic solvents, such as collidine and butanol, be used, but the complex-forming reagent also can be changed. The large number of suitable organic solvents and complexing reagents available makes possible a very large number of two-way separations; one of these is illustrated in figure 4, and a number of others have been reported.

The anion associated with the cation in the original metallic salt does not always move to the same position on the paper as the cation, unless it becomes bound to the latter by complex formation. With some mobile phases it is found that the separations of the cations are not affected by the anions present, provided that no completely insoluble salt is formed. On the other hand, it may sometimes be an advantage to have an anion present which will immobilize some of the cations but allow others to move. This idea has been

TABLE III

Abridged schemes of analysis illustrated in figure 3

Several chromatograms of the same mixture are prepared simultaneously, and then treated separately for analysis.

(*a*) *Ag, Pb, Ni, Cu, Sb, Ba* (*figure 3a*)
- (i) Sprayed with potassium chromate and then treated with sulphur dioxide gas. Pb—yellow; Ag—red.
- (ii) Strip from (i) held over ammonia. Ag spot fades. Sprayed with rhodizonic and then dilute hydrochloric acid. Ba—red; Pb—violet; Ag—grey.
- (iii) Fresh strip sprayed with rubeanic acid and then held over ammonia. Ni—blue; Cu—olive green.
- (iv) Fresh strip sprayed with ammonium sulphide, treated with concentrated hydrochloric acid to dissolve sulphides, and then sprayed with phosphomolybdic acid. Sb—royal blue.

(*b*) *Al, Cu, As, Sn* (*figure 3b*)
- (i) Sprayed with sodium hypophosphite in dilute hydrochloric acid and warmed. As—brown. Then treated with kojic acid—8-hydroxyquinoline spray, held over ammonia, and viewed under ultra-violet light. Al—green fluorescence; Sn—yellow fluorescence. Cu and As—dark, non-fluorescent.
- (ii) Sprayed with hypophosphite to show As, then with rubeanic acid and held over ammonia. Cu—olive-green.

(*c*) *Al, Na, U, Fe, Sn* (*figure 3c*)
- (i) Sprayed with potassium ferrocyanide. U—brown; Fe—blue.
- (ii) Sprayed with zinc uranyl acetate in acetic acid. Na—bluish-green fluorescence under ultra-violet light. Dark spots—Fe, U, and Sn.
- (iii) Treated with kojic acid and 8-hydroxyquinoline spray, held over ammonia, and viewed under ultra-violet light. Al—green fluorescence; Sn—yellow fluorescence; Dark spots—U and Fe.

NOTE. Full details for the analysis of unknown mixtures can be found in reference [12].

applied to the separation of arsenic from other cations by having as the mobile phase a butanol-water mixture containing ammonium borate, ammonium tartrate, and mannitol, so preventing the other cations from moving. Another aspect of the same idea is used for one of the analytical schemes, when the initial spots on the paper are given a spray with sodium hypobromite and acetic acid to prevent manganese, cobalt, nickel, and some other cations moving with the butanol-benzoylacetone mixture.

Anion analysis has not been closely investigated, although a number of separations have been reported [10–12], and an example of the kind of chromatogram which can be obtained is shown in figure 5. These chromatograms were prepared with a mixture of fifteen parts by volume of butanol, fifteen parts of water, eight parts of pyridine, and one part of 0·88 ammonia as the mobile phase. The following anions were identified: chromate, chloride, and bromide by spraying with silver nitrate and exposing to ultra-violet light; iodide and thiocyanate by spraying with ferric alum. Experiments show that the R_f of the anion is usually independent of the cation with which it is initially associated, and that if the free acid is used it moves with the same R_f. One can, however, visualize cases in which the cation might interfere, so that it is advisable to start with the sodium salts, as is usually done in qualitative analysis.

The separations achieved by paper chromatography can be utilized for quantitative analysis both on the micro-scale and in quantities of up to one gram [10–14]. With micro-quantities the separations can be carried out on a sheet of paper arranged as illustrated in figure 6(*b*). The portions of the paper containing the respective cations are cut out after separation is complete, and then independently extracted with an apparatus like that illustrated in figure 6(*c*). Such a procedure can be used whenever sufficient separation occurs. Similar schemes have been suggested by other workers. The extracted cations may be estimated by a colorimeter or polarograph. For larger quantities, columns of cellulose or thick strips of filter-paper pulp can be used. The separated fractions, as they come through the column, can then be collected in tubes, using the automatic fraction collector [15], as illustrated in figure 6(*a*). These procedures can also be used for preparative work, though no serious use of this fact has as yet been reported; it is, however, an obvious line of development.

In the few years that have elapsed since serious attention was first given to paper chromatography of inorganic compounds, it has been shown that it is likely to be a very useful technique in all fields of science where analysis is needed. Apart from the obvious applications, it may well solve some of the problems associated with the detection and estimation of trace-metals, though some preliminary concentration on an ion-exchange column may first be needed. In inorganic chemistry itself, it will serve to stimulate interest in the extraction of minute quantities of individual metals such as are found in the rare earths, in the preparation and separation of inorganic complexes, and in many problems which have lain dormant for years because of the difficulties of analysis.

(The chromatograms were prepared by Messrs. H. M. Stevens, B. Ellis, and C. D. Bamberger.)

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Book reviews

CHROMATOGRAPHY

Adsorption and Chromatography, *by Harold Gomes Cassidy. Pp.* 360, *with many line diagrams. Interscience Publishers Inc., New York and London.* 1951. 56*s. net.*

This book is a summary of the principles underlying the various methods of analysis—based on adsorption, ion-exchange, and partition—known collectively as chromatography. The author has prepared the text well and added greatly to its value by a detailed bibliography and comprehensive author and subject indexes. The book is valuable not only for summarizing what we know of the physico-chemical principles governing the various chromatographic techniques but for revealing the wide gaps which still exist in our knowledge; one may, however, take some consolation in the recently expressed opinion of Zechmeister that theoretical studies have hitherto had little influence on the practical use of chromatography.

The claim made on page 207, that 'chromatography was invented by Tswett in 1906,' is no longer universally accepted; the prior claims of Day, whose experiments were at once followed up by Engler and Albrecht and others, have certainly hitherto been too lightly dismissed. Furthermore the claim that Schoenbein (page 313) discovered capillary analysis may be challenged by that of Runge. These points are of academic interest, in no way detracting from the practical value of the present book, but it is to be hoped that a detailed study will be made of the early, and today almost completely unknown or ignored, literature of chromatography.

SOME LANGMUIR PAPERS REPUBLISHED

Phenomena, Atoms, and Molecules, *by Irving Langmuir. Pp. xi* + 436, *with several line diagrams. Philosophical Library, New York.* 1950. $10 *net.*

The introduction to this book tells briefly of the conditions under which the author has worked for more than forty years in the research laboratories at Schenectady of the General Electric Company. These laboratories had been established to carry out fundamental research 'in broad fields associated with the work of the company.' Dr Langmuir has published about two hundred papers, which are listed in a bibliography contained at the end of the book. The present volume contains twenty of these papers. They range from the philosophy of scientific work to some of his fundamental contributions to surface physic and chemistry.

It is not easy to understand the basis on which this particular choice has been made. Some of the papers included are lectures given before scientific societies on special occasions; others are of a general review nature; others again are detailed accounts of particular research problems. There appears to have been no attempt to edit them for publication. In different chapters differing symbols are used for the same physical quantity; sometimes the references appear as footnotes, at others they are collected at the end of the chapter—apparently according to the usage of the scientific journal in which the chapter originally appeared as a paper. Similar confusions, which arise from failure to edit the papers, abound throughout the collection. On the dust cover, the publisher refers to this as Dr Langmuir's 'first book.' Such a collection of reprinted and unedited papers hardly warrants that description.

An account of Dr Langmuir's classical researches, written by him today in the light of present knowledge, could be a valuable and stimulating book. Awareness of what could have been done only makes the present collection of reprints the more disappointing. A. R. MILLER

VERTEBRATE LIFE

The Life of Vertebrates, *by J. Z. Young. Pp.* 767, *with numerous line diagrams. Oxford University Press, London.* 1950. 42*s. net.*

To produce a textbook that is at once thoroughly readable and thoroughly usable demands sympathetic outlook, imagination, and literary capacity. It is therefore small wonder that able textbook writers are rarer than able investigators. For comprehensiveness, philosophic grasp, humanity, and the pleasure that it will give the not overspecialized reader, Professor Young's book is, in its department, the most successful effort of the kind that the century has yet yielded. It will do much to determine the direction of zoological class-teaching, which has long shown signs of needing change.

Professor Young's book naturally invites comparison with the excellent standard volume on vertebrates by Parker and Haswell, originally issued in 1898 and now in its sixth edition. This retains its value as the first reference work for the student on matters of morphological fact, since it is fuller and has more illustrations. In every other respect Professor Young's is the superior. It is conceived on a more generous plan, and, though less detailed, is much more comprehensive, notably in its treatment of the geological record. Moreover, Professor Young is concerned with animals as living wholes, with their habits, their bionomics and ecologies, their psychologies, their successes and failures in the struggle for life, and the differentiations and origins of their various physiological systems. His book is thus peculiarly suited to such medical men as are properly interested in that odd vertebrate *Homo sapiens.* In dealing with that species he dwells on certain of its primitive or, rather, infantile features, thanks to which it accommodates itself to the most different environments and is thus exterminating an increasing number of other vertebrate species.

The history of textbooks necessarily reflects the changing interests of the times. For a hundred years from Cuvier—that is, throughout the nineteenth century—zoological textbooks concentrated on comparative anatomy with an increasing stress on development. All this was intensified during the high Darwinian tide. Even the vertebrate manual of T. H. Huxley (1871) was purely morphological. In the classical zoological textbooks of the age, as Professor Young points out, discussion of other aspects was either avoided or relegated to appendices. A change came in the twentieth century with the rise of experimental embryology, biochemistry, comparative physiology, and ecology, but Professor Young is the first to construct a synoptic view of the results attained in all these, and he has combined this with due treatment of important conclusions in palaeontology, comparative psychology, and, above all, with the perennially refreshing old-fashioned natural history. We miss, however, any but the lightest references to genetics. Mammalian structure will be more fully discussed, he tells us, in a second volume, which will also include a survey of comparative embryology. This will surely be welcome, for comprehensive manuals on the study of mammals

are antiquated and inadequate, and reference is still not infrequently necessary to Owen's classic of 1866—a hiatus of an extent probably unique in the range of science textbooks.

The illustrations of Professor Young's volume are mostly excellent. We would draw attention to some of those by Miss E. T. Tarlington of the great apes and of the horses. They rival the well-known figures of reptiles with which the late Miss M. E. Durham adorned the Cambridge Natural History, though the work of neither compares in beauty or perhaps in exactness to many of the masterpieces of zoological wood-engraving issued by the London house of Van Voorst in the fifties and sixties of the last century. Nevertheless, the figures exhibit care and feeling. Their clarity, and the skill used in designing them, make us regret the more that the explanations of too many details are relegated to captions. This fatiguing and outmoded device is defensible for conventional abbreviations, as for well-known bones, for parts of the brain, for the great vessels, and so on. In most anatomical figures, however, the name of each relevant part should be plainly printed on it. This method is of respectable antiquity and, since the first edition of Gray's *Anatomy* in 1858, has become universal so far as figures of the human subject are concerned. The sooner it is generally accepted for zoological textbooks the more the student's time and temper will be saved. Some of the figures are rather crowded, and the index should be fuller. All these are minor defects in a major work that is truly delightful and humane. Where nearly everything is good, we would select the section on fishes as attaining the rank of a masterpiece in its own *genre*.

CHARLES SINGER

THE USE OF WOOD

The Coming Age of Wood, *by Egon Glessinger. Pp.* 279, *with several illustrative charts. Martin Secker and Warburg Limited, London.* 1950. 12*s.* 6*d. net.*

The author of this book, who for many years before the war was Secretary General of the *Comité International du Bois*, and is now head of the Forest Products branch of F.A.O., writes with unbounded enthusiasm about the possibilities of increasing the yield of raw materials for industry from the forests of the world.

In the first part of the book emphasis is laid on the need for better conservation of the existing forests, and for replacement of wasteful methods of timber 'mining' by the sustained yields of managed forest. This part ends with a chapter on the role of wood in world politics, summarized from an earlier book by the same author.

The second part consists of a pictorial representation, in much simplified diagrammatic form, of the basic principles of forestry, and of the waste involved in various forms of conversion and utilization.

The third part is devoted to various aspects of timber utilization, with particular emphasis on the use of wood as a raw material for chemical processes. The author stresses the importance of finding uses for lignin, which he describes as the enigmatic key to wood-chemistry, and which represents more or less a dead loss to the industries extracting cellulose from wood.

The theme running through the book is integrated utilization—that is, each industry should use that part of the tree most suited to its particular purpose, leaving the residue to be worked up by another process into a different product, the ideal being complete utilization of the tree, instead of the 25 per cent. and 35 per cent. which he estimates are achieved today by the sawmilling and pulping industries respectively.

While it is refreshing to read a book written with such zest, the author's enthusiasm sometimes runs away with him, and he tends to gloss over some of the difficulties involved. Nevertheless the book should do good by bringing home to the general reader the imperative need for husbanding the forest resources of the world, and for utilizing them to the fullest advantage.

W. P. K. FINDLAY

THE GROWTH AND UNITY OF SCIENCE

A Century of Science, 1851–1951, *by specialist authors under the editorship of Herbert Dingle. Pp.* 338. *Hutchinson's Scientific and Technical Publications, London.* 1951. 15*s. net.*

This book has been issued in order to summarize and assess scientific progress during the period between the Great Exhibition and the Festival of Britain. It opens appropriately with four chapters on physical aspects of science (the concept of energy, field physics, particle physics, the structure of the atom), and leads on through chemistry (the structure of molecules, the chemical elements) to geology and the earth's atmosphere. Accounts of the constitution and evolution of stars and the structure of the universe complete the first half of the book.

Discussions of organic evolution, the coming of man, and the progress of *Homo sapiens* are followed by others dealing with the development of genetics, embryology, physiology, histology, and biochemistry. Finally, a review of progress in medicine is linked with an account of the growth of psychology. Each subject has been undertaken by an eminent authority in such a way as to present a readable conspectus of the enormous scientific advances of the last hundred years, to which British men of science have made so great a contribution. Professor Dingle's thought-provoking preface and closing chapter emphasize the extension and unification of science during the period under review, the obliteration of arbitrary boundaries between such branches as botany, zoology, and entomology, and the breakdown of the nineteenth-century view of science.

A short account of so vast a subject necessarily tends to become sketchy, as is evident for example in the slight treatment of organic chemistry; but the book will interest intelligent readers having a general acquaintance with science, and it should be of value in helping scientific specialists to view their own work in a proper perspective.

JOHN READ

A CONTRIBUTION TO THE HISTORY OF CHEMICAL INDUSTRY

A History of the Chemical Industry in Widnes, *by D. W. F. Hardie. Pp.* 250, *with* 38 *plates. Imperial Chemical Industries Limited, London.* 1950. 21*s. net.*

The two major chemical alkali processes were the Leblanc and ammonia-soda processes and their many ramifications. The electrolytic process could not develop until cheap electrical energy was available. Dr Hardie tells in a very interesting way the story of the evolution of the industry in Widnes. The great names of Muspratt, Gossage, Deacon, Gaskell, Mond, Brunner, Hargreaves, and Hurter come into the account, and the success of the industry was due to the fortunate combination of scientific and business abilities of high order in the different men concerned. The early Leblanc process, much improved in Britain, wasted chlorine and sulphur. The chlorine was recovered by Weldon and Deacon; thousands of tons of sulphur in the form

of alkali waste were buried under Widnes or heaped into mounds until Chance perfected the sulphur-recovery process.

It is impossible in a few lines to do justice to the story so well told in this book, which deals both with the scientific and technical and with the social and economic aspects of the industry, bringing the account to modern times. Though there is a large literature not mentioned by the author, unpublished material has been drawn upon and the result is a connected and easily understood narrative. The portraits and illustrations of plant are admirable, and the general style is appropriate to the subject. This is a book which fully justifies all the time and labour that must have been spent on its production, and will be of interest to academic as well as industrial chemists.

J. R. PARTINGTON

POPULAR MATHEMATICS

Mathematics and the Imagination, *by Edward Kasner and James Newman. Pp.* 380, *with numerous line diagrams. G. Bell and Sons Limited, London.* 1949. 15*s. net.*

This is a canvas on which the authors have painted many and diverse scenes. From transfinite numbers to topology, from the googolplex to doughnuts, from transcendental numbers to non-Euclidean geometries, from the calculus to mathematical paradoxes and puzzles, they open our eyes to a succession of imaginative vistas. They delineate these varied scenes with skill and an understanding of the average reader's equipment; their treatment is always fresh and stimulating.

The choice of topics dealt with in this book differs from that in most popular books about mathematics. Such books generally try either to give a philosophical discussion of the concepts of mathematics or to present again, in terms of everyday things, the elementary mathematics that most of us happily forgot as soon as we had cleared the hurdle of school certificate. On the other hand, in this book the authors introduce those topics which are at present the subject of mathematical thought and research. Many of these topics have their origin in apparently simple puzzles and paradoxes. The authors make full use of the opportunity which this approach provides to explain their essence to the non-mathematical reader, and to show how the apparently simple may be, in fact, subtle and replete with new ideas.

Diverse as are the scenes presented to our view, they have a unifying idea. They are all concerned with that mathematical realm where the processes of thought are nearer those of the poet than the scientist; where—without losing its austere logical form—mathematics becomes supreme art as well as science, leading the creative faculties beyond even imagination and intuition.

A. R. MILLER

NUCLEAR CHEMISTRY

Principles of Nuclear Chemistry, *by Russell R. Williams. Pp.* x + 307. *Macmillan and Company Limited, London.* 1950. *D. van Nostrand Company Inc., New York.* 28*s.* 6*d.* ($3.75) *net.*

The author's intention is clearly expressed by the title: the book lays emphasis on principles, not on discussion of details. It covers a wide range of subjects, some of which belong more to nuclear physics than to nuclear chemistry, as, for instance, cascade transformers, van de Graaf generators, and cyclotrons; a description of the preparation of radium-beryllium neutron sources would perhaps have been of greater use to those working in a chemical laboratory. The concentration of isotopes is discussed at some length; it is unfortunate that for the separation by thermal diffusion the formula given by S. Chapman in his very first paper (1919) is quoted, and the fact that a corrected form was published in various papers between 1922 and 1929 is overlooked.

The chemical part comprises chapters on the laboratory treatment of radioelements, the chemical and biological effects of radiations, geological age determinations, tracer studies, and related subjects. Discussing the radiocolloids, the author states that it is now 'generally assumed' that their formation is due to adsorption on solid particles suspended in the liquid phase; in view of the very scanty evidence in favour of this explanation it is to be hoped that some dissenters will continue to challenge it. The table of the periodic system is rather confusing owing to the complete merging of the sub-groups; the symbol of the element Francium is here and in various other places written as Fa, instead of the internationally accepted Fr.

At the end of several chapters numerical exercises and lists of papers for supplementary reading are given. As a smoothly written introduction into a vast field the book will be found useful.

F. A. PANETH

HETEROCYCLIC COMPOUNDS

Heterocyclic Compounds, Volume I. *Editor-in-chief, R. C. Elderfield. Pp. vii* + 703. *John Wiley and Sons, New York; Chapman and Hall Limited, London.* 1950. £6 *net.*

The rapidly expanding knowledge of organic chemistry has made the provision of a series of volumes in all branches of the subject a matter of urgency. This need has perhaps been most keenly felt in the field of heterocyclic compounds, where so much important work has been done in recent years, and its reality is shown by the almost simultaneous appearance of the present volume and a monograph 'The Heterocyclic Derivatives of Phosphorus, Arsenic, etc.' by F. G. Mann in the series 'Heterocyclic Compounds,' edited by A. Weissberger and published by Interscience Publishers, New York.

The present book deals with three-, four-, five-, and six-membered monocyclic compounds containing one hetero atom, either oxygen, nitrogen, or sulphur. These twelve groups are described in eight chapters by separate authors: ethylene and trimethylene oxides; ethyleneimine; trimethyleneimine; furan; thiophen; pyrrole; pyrans, pyrones, thiapyrans and thiapyrones; pyridine, piperidine, and partially reduced pyridines. The chapters reach a very high standard, and although not intended to be completely comprehensive, they give an excellently detailed, up-to-date picture of modern knowledge. They are much more than compilations of facts, and are attractive to read. The very large number of references—something over 3000—makes the book of the greatest value to research workers. The subjects are reviewed from established modern viewpoints, and are illustrated by excellent graphic formulae. This book, in spite of its high price, will find its way to the shelves of most research workers, and the appearance of other volumes (unnumbered) in the series is awaited with interest. Future volumes should be provided with author indexes.

W. BAKER

Some books received

(*Note.* Mention of a book on this page does not preclude subsequent review.)

BIOCHEMISTRY

Introduction to Agricultural Biochemistry, *by R. Adams Dutcher, Clifford O. Jensen, and Paul M. Althouse. Pp.* 502. *John Wiley and Sons Inc., New York; Chapman and Hall Limited, London.* 1951. 48*s. net.*

The Vitamin B Complex, *by F. A. Robinson. Pp.* 668. *Chapman and Hall Limited, London.* 1951. 60*s. net.*

BIOLOGY

Insects and Hygiene, *by J. R. Busvine. Pp.* 482, *with numerous line diagrams. Methuen and Co. Limited, London.* 1951. 30*s. net.*

CHEMISTRY

Bibliography of Standard Tentative and Recommended or Recognized Methods of Analysis. *Compiled under the authority of the Analytical Methods Committee of the Society of Public Analysts and other Analytical Chemists. Pp.* 221. *W. Heffer and Sons, Cambridge.* 1951. 25*s. net.*

The Chemical Analysis of Waters, Boiler- and Feed-Waters, Sewage, and Effluents, *by Dennis Dickinson. Pp.* 143, *with line diagrams. Blackie and Sons Limited, London. Second edition.* 1950. 6*s.* 6*d. net.*

The Chemistry of Hydrazine, *by L. F. Andrieth and Betty Ackerson Ogg. Pp.* 244. *John Wiley and Sons Inc., New York; Chapman and Hall Limited, London.* 1951. 40*s. net.*

The Chemistry of Nonbenzenoid Hydrocarbons, *by Benjamin T. Brooks. Pp.* 615, *with numerous line diagrams. Reinhold Publishing Corporation, New York; Chapman and Hall Limited, London. Second edition.* 1951. 96*s. net.*

Intermediate Practical Chemistry, *by Sylvanus J. Smith. Pp.* 248, *with numerous line diagrams. Macmillan and Co. Limited, London.* 1951. 8*s. net.*

Organophosphorus Compounds, *by Gennedy M. Kosolapoff. Pp.* 376. *John Wiley and Sons Inc., New York; Chapman and Hall Limited, London.* 1951. 60*s. net.*

The Structure of Physical Chemistry, *by Sir Cyril Hinshelwood. Pp.* 476, *with several line diagrams. Oxford University Press, London.* 1951. 35*s. net.*

COSMOGONY

The Primeval Atom, *by Georges Lemaître. (Translated by Betty H. Korff and Serge A. Korff.) Pp.* 186. *D. Van Nostrand Co. Inc., New York; Macmillan and Co. Limited, London.* 1951. 22*s.* 6*d. net.*

CRYSTALLOGRAPHY

Crystal Growth, *by H. E. Buckley. Pp.* 571, *with numerous line and half-tone illustrations. John Wiley and Sons Inc., New York; Chapman and Hall Limited, London.* 1951. 72*s. net.*

GENERAL SCIENCE

British Scientists, *by E. J. Holmyard. Pp.* 88, *with several half-tone illustrations. J. M. Dent and Sons Limited, London.* 1951. 6*s. net.*

The Common Sense of Science, *by J. Bronowski. Pp.* 154. *William Heinemann, London.* 1951. 8*s.* 6*d. net.*

A Dictionary of Science, *by E. B. Uvarov and D. R. Chapman. Pp.* 240. *Penguin Reference Books, Harmondsworth, Middlesex. New edition.* 1951. 2*s. net.*

Laboratory Design, *edited by H. S. Colman. Pp.* 393, *with numerous half-tone and line illustrations. Reinhold Publishing Corporation, New York; Chapman and Hall Limited, London.* 1951. 96*s. net.*

The Physical Basis of Life, *by J. D. Bernal. Pp.* 80. *Routledge and Kegan Paul, London.* 1951. 6*s. net.*

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